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NOTE.—The First, Second and Third Reports of the Committee on the Heterogeneity of Steel Ingots were originally printed in the *Journal of The Iron and Steel Institute* as follows :

First Report : 1926, No. I., pp. 39–151.

Second Report : 1928, No. I., pp. 401–547. Price 16/-. (Members, 10/-.)

Third Report : 1929, No. I., pp. 305–376. Price 10/-. (Members, 5/-.)

Reprints of the Second and Third Reports are still available, but the First Report is out of print.

LIST OF TRANSLATIONS ISSUED BETWEEN 1st JUNE and 31st DECEMBER, 1943.

(For earlier translations see notice in the No. I. Journal for 1943.)

Price: Nos. 1 to 27 gratis; others 10s. for the first copy, 5s. for each additional copy of the same translation.

- No. 138 (German). H. HAUSEN: "The Calculation of Heat Transfer in Regenerators." (*Verfahrenstechnik, Zeitschrift des Vereines deutscher Ingenieure, Beiheft*, 1942, No. 2, pp. 31-43).
- No. 139 (German). E. SENFTER: "Increasing Blast-Furnace Efficiency with a Simultaneous Saving of Coke." (*Stahl und Eisen*, 1942, vol. 62, Dec. 10, pp. 1041-1052).
- No. 140 (German). E. SIEBEL and R. KOBITZSCH: "The Heating of Wire while it is being Drawn." (*Stahl und Eisen*, 1943, vol. 63, Feb. 11, pp. 110-113).
- No. 141 (German). M. VON POHL: "The Corrosion of Pipes and Tanks by Mineral Oil and Petroleum Gases and Its Prevention." (*Korrosion und Metallschutz*, 1942, vol. 18, pp. 311-321).
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- No. 143 (German). E. PIWOWARSKY: "The Effect of Ladle Additions on the Properties of Cast Iron." (*Giesserei*, 1940, vol. 27, Jan. 26, pp. 21-30; Feb. 9, pp. 47-52). (Made available through the courtesy of the British Cast Iron Research Association).
- No. 144 (German). E. PIWOWARSKY: "Ladle Additions to Cast Iron." (*Giesserei*, 1940, vol. 27, Apr. 5, pp. 124-125). (Made available through the courtesy of the British Cast Iron Research Association).
- No. 145 (German). K. ENDELL, H. REININGER, H. JENSCH and P. SCAKI: "The Importance of the Swelling Properties of Clay Binders for Foundry Sands." (*Giesserei*, 1940, vol. 27, Nov. 29, pp. 465-475; Dec. 3, pp. 499-502). (Made available through the courtesy of the British Cast Iron Research Association).
- No. 146 (German). H. J. WIESTER: "Steels for Use at Low Temperatures and Their Testing." (*Stahl und Eisen*, 1943, vol. 63, Jan. 21, pp. 41-47; Jan. 28, pp. 64-68. Discussion, pp. 69-74).
- No. 147 (German). G. TRÖMEL: "Investigations of the Ternary System $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ and their Importance in the Production of Basic-Bessemer Slags." (*Stahl und Eisen*, 1943, vol. 63, Jan. 14, pp. 21-30).
- No. 148 (Swedish). H. WOLFF: "Developments in the Production of Hard Metals." (*Teknisk Tidskrift*, 1941, vol. 71, Dec. 27, pp. 549-551).
- No. 149 (German). HERMANN DEHLER: "Compacted Magnets with a Synthetic Resin Binder." (*Stahl und Eisen*, 1942, vol. 62, Nov. 19, pp. 983-986).
- No. 150 (German). W. LUEG: "Temperature and Energy Conditions when Drawing through Multiple Dies." (*Stahl und Eisen*, 1943, vol. 63, Feb. 11, pp. 113-114).
- No. 151 (German). W. DAWIHL: "The Scientific and Technical Principles of Powder Metallurgy and Its Sphere of Application." (*Stahl und Eisen*, 1941, vol. 61, Oct. 2, pp. 909-919).

- No. 152 (German). F. WESEMANN: "Investigations and Proposals for the Better Control of Mill Furnaces." (*Stahl und Eisen*, 1930, vol. 50, Nov. 13, pp. 1601-1610). (Translated by Mr. W. Goldsbrough, submitted through the Industrial Furnaces Research Committee and made available by courtesy of the Lancashire Steel Corporation, Ltd.).
- No. 153 (Swedish). H. NATHORST: "The Manufacture of Tool Steel in the United States." (*Jernkontorets Annaler*, 1941, vol. 125, No. 12, pp. 653-694).
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- No. 155 (German). H. WIEGAND: "Effect of Surface Treatment on Fatigue Strength." (*Oberfläche und Dauerfestigkeit*. Berlin-Spandau 1940: BMW Flugmotorenbau). (Made available through the courtesy of the Ministry of Aircraft Production, R.T.P. No. 1772).
- No. 156 (German). W. OELSEN and H. MAETZ: "The Behaviour of Fluor-spar and of Calcium Phosphates in Relation to the Ferrous Oxide in the Melt and Its Metallurgical Significance." (*Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1941, vol. 23, No. 12, pp. 195-245).
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- No. 158 (German). W. BAUKLOH, F. SCHULTE and H. FRIEDERICH: "A Study of the Processes Involved in the Malleablising of Unalloyed and Alloyed Cast Iron in Carbon-Monoxide/Carbon-Dioxide Mixtures." (*Archiv für das Eisenhüttenwesen*, 1943, vol. 16, Mar., pp. 341-354). (Printed).
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- No. 160 (German). E. ROHDE: "Substitute Materials in Steelworks Machinery (in Germany)." (*Stahl und Eisen*, 1943, vol. 63, Feb. 4, pp. 85-94). (Printed).
- No. 161 (German). A. KRISCH: "The Creep Strength of Steel at Room Temperature." (*Archiv für das Eisenhüttenwesen*, 1942, vol. 15, June, pp. 539-542). (Printed).
- No. 162 (German). A. GOTTA and H. SEEHOF: "The Nessler Reaction and Its Use in the Determination of Nitrogen in Commercial Ferrous Alloys." (*Zeitschrift für analytische Chemie*, 1942, vol. 124, pp. 216-226). (Printed).
- No. 163 (Russian). YU. GRDINA and N. SHUBINA: "The Gas-Hardening of Rail Ends." (*Stal*, 1940, Oct., pp. 40-44). (Printed).
- No. 164 (German). K. H. HENNENBERGER: "The Decomposition of Raw Phosphate by Smelting with Soda Slag." (*Stahl und Eisen*, 1939, vol. 59, June 1, pp. 662-663). (Printed).
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- No. 166 (German). F. RAPATZ: "The Application Possibilities of Stainless and Heat-Resisting Steels Containing Nitrogen Additions." (*Stahl und Eisen*, 1941, vol. 61, Nov. 27, pp. 1073-1078). (Translated by Mr. W. B. Jones and made available through the courtesy of Tube Investments, Ltd.). (Printed).

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PREFACE.

THE present volume contains one report and thirteen papers presented at the Autumn Meeting of the Institute held in London on October 14th, 1943; of these, the report and six papers were presented under the auspices of the Joint Research Committees of the Institute and the British Iron and Steel Federation. The discussions and correspondence to which these give rise are also included, together with the authors' replies. In addition, the author's reply to the discussion on a paper included in the No. I. volume of the *Journal* for 1943 will be found in the present book.

The foregoing papers, together with the Minutes of Proceedings of the Meeting and biographical notes on deceased Members are included in Section I. of this *Journal*.

Section II. is devoted to a survey of the literature on the manufacture and properties of iron and steel, and kindred subjects, and consists of a collection of abstracts of articles from the Transactions and Proceedings of scientific societies and from the technical press. This Section also contains reviews of recent books and bibliographies of literature dealing with the manufacture and properties of iron and steel. The matter included in this Section has already appeared in the *Bulletin of The Iron and Steel Institute*, which is issued monthly.

In front of the title page are inserted lists of Bibliographies, Special Reports and Translations issued by the Institute.

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February 29th, 1944.

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ABBREVIATIONS USED IN TEXT.

Å.	Ångström unit(s).	kg.cal.	kilogramme-calory ; -calories.
A.C.	air-cooled ; alternat- ing cur- rent.	kg.m.	kilogramme-metre(s).
A.H.	air-hardened.	km.	kilometre(s).
amp.	ampère(s).	kVA.	kilovolt-ampère(s).
amp.hr.	ampère-hour(s).	kW.	kilowatt(s).
atm.	atmosphere(s) (pressure).	kWh.	kilowatt-hour(s).
Bé.	Baumé (scale).	lb.	pound(s).
b.h.p.	brake horse-power.	L.F.	low-frequency.
B.o.T.	Board of Trade.	m.	metre(s).
B.Th.U.	British thermal unit(s).	m.amp.	milliampère(s).
C.	centigrade (scale).	mV.	millivolt(s).
cal.	calory ; calories.	max.	maximum.
c.c.	cubic centimetre(s).	mg.	milligramme(s).
c.d.	current density.	min.	minimum ; minute(s).
c.g.s.	centimetre-gramme-second unit(s).	ml.	millilitre(s).
cm.	centimetre(s).	mm.	millimetre(s).
coeff.	coefficient.	m.m.f.	magnetomotive force.
const.	constant(s).	N.	normal (solution).
c.p.	candle-power.	N.T.P.	normal temperature and pressure.
cu.	cubic.	O.H.	open-hearth ; oil-hardened.
cwt.	hundredweight(s).	O.Q.	oil-quenched.
D.C.	direct current.	oz.	ounce(s).
dia.	diameter(s).	p.d.	potential difference.
dm.	decimetre(s).	pH	hydrogen-ion concentra- tion.
e.m.f.	electromotive force.	r.p.m.	revolutions per minute.
F.	Fahrenheit (scale).	sec.	second(s).
ft.	foot ; feet.	sp. gr.	specific gravity.
ft.lb.	foot-pound(s).	sq.	square.
g.	gramme(s).	T.	tempered.
gal.	gallon(s).	temp.	temperature.
H.F.	high-frequency.	V.	volt(s).
h.p.	horse-power.	VA.	volt-ampère(s).
h.p.hr.	horse-power-hour(s).	Wh.	watt-hour(s).
hr.	hour(s).	W.G.	water gauge.
in.	inch ; inches.	W.Q.	water-quenched.
in.lb.	inch-pound(s).	yd.	yard(s).
K.	absolute temperature (Kel- vin scale).	°	degree(s).
kg.	kilogramme(s).		

SECTION I.

*MINUTES OF PROCEEDINGS
AND PAPERS OF
THE IRON AND STEEL INSTITUTE.*

AUTUMN MEETING

1943

MINUTES OF PROCEEDINGS

AND

PAPERS AND DISCUSSIONS

AT THE

AUTUMN MEETING IN LONDON, 1943.

THE AUTUMN MEETING OF THE IRON AND STEEL INSTITUTE was held at the Offices of the Institute, 4 Grosvenor Gardens, London, S.W.1, on Thursday, October 14, 1943, the PRESIDENT (Mr. James Henderson) being in the Chair. There were two sessions, commencing at 11.0 A.M. and 2.45 P.M., respectively.

The Minutes of the previous Meeting were taken as read and signed.

OBITUARY.

The PRESIDENT (Mr. James Henderson): Within the last few days, our industry has sustained a very serious loss by the death of Sir Robert Hilton, which took place last Sunday, October 10. I am happy to feel that almost up to the last he was able and willing, as always, to do all he could to forward the interests of the iron and steel industry.

I do not propose to give here a sketch of his career, which is known to many of you. From early years he was marked out for promotion, and the later years of his life were spent as Managing Director and finally as Vice-Chairman of The United Steel Companies, Ltd. I was privileged to serve under him, so that I can speak at first hand of the great qualities which he possessed, and which he used to the fullest extent in administration and organisation. He was also a warm supporter of the scientific side of the industry, and was very helpful to us in this Institute. He supported research both in his own companies and in the industry. We have lost a good friend and a great captain of industry—no one deserved that title better than he did. I am sure you would wish to record our sympathy with his widow and family, and will ask the Secretary to send them a suitable letter.

The Members stood in silence for a few moments as a tribute of respect.

CHANGES ON THE COUNCIL.

President-Elect for 1944.

The PRESIDENT : It gives me great pleasure to tell you that the Council at their meeting this morning decided to nominate Mr. Arthur Dorman to succeed me as President of the Institute. I was rash enough to ask the Secretary to prepare for me a list of some of his activities, and I have it here, but it is much too long to read ! Apart from his association with Messrs. Dorman Long & Co., Ltd., and many other companies, he is a Vice-President of the Federation of British Industries, Past-President of the National Federation of Iron and Steel Manufacturers¹ and of the National Confederation of Employers' Organisations, and has been a Member of this Institute since 1908 ; he became a Member of Council in 1925 and a Vice-President in 1932. I do not think that we could wish for a more experienced and distinguished occupant of this Chair. (*Applause.*)

Mr. ARTHUR DORMAN (President-Elect) : I should like to thank the Council and the Institute for the way in which this nomination has been received. I am very modest in accepting it, because my technical qualifications are meagre. We have to remember that the world to-day is very research-minded, and that there are great possibilities in front of this Institute. When one looks back at the distinguished men who have filled the office of President of the Institute, it must make anyone who is not specially endowed with technical knowledge a little nervous about occupying it. I can, however, promise you that I will do my best to maintain the reputation of The Iron and Steel Institute, and I hope that I shall not fail in achieving that aim. (*Applause.*)

Vice-Presidents and Members of Council retiring in 1944.

The SECRETARY (Mr. K. Headlam-Morley) announced that, in accordance with Bye-Law No. 10, the following Vice-Presidents and Members of Council would retire in rotation at the Annual General Meeting in 1944 :

Vice-Presidents.—Dr. W. H. Hatfield, F.R.S.,² Sir William Larke, K.B.E., and Mr. C. E. Lloyd, M.P.

Members of Council.—Principal C. A. Edwards, F.R.S., Mr. G. H. Latham, Mr. E. F. Law, Mr. R. Mather, Sir Arthur Winder and Mr. N. H. Rollason.

He also announced that Mr. Bernard Thomas and Provost J. Tennent had succeeded Mr. Albert Wright and Colonel Alan Stein as Presidents respectively of the Staffordshire Iron and Steel Institute and of the West of Scotland Iron and Steel Institute, and had accepted invitations to succeed them also as Honorary Members of Council during their periods of office.

¹ Now the British Iron and Steel Federation.

² Died October 17, 1943. For obituary see p. 721 p.

LEGACY FROM THE LATE SIR ROBERT HADFIELD.

The PRESIDENT : The late Sir Robert Hadfield left a legacy of £250 to the Institute, and the money has now been paid into our funds. Its utilisation is left to the discretion of the Council. It is difficult at the present time to decide upon the best way of dealing with this money and accordingly it has been invested. The use to be made of it will be brought up again in a year or two's time. We are glad to think that Sir Robert Hadfield remembered the Institute, which in his lifetime he had helped so much by his work.

MR. J. H. WHITELEY, BESSEMER GOLD MEDALLIST FOR 1943.

In calling upon Mr. J. H. WHITELEY to present his paper on "A Study of Austenitic Grain Growth in Medium-Carbon Steels" (see p. 513 P), the PRESIDENT (Mr. James Henderson) said : In calling upon Mr. Whiteley to present his paper, I should like to refer to the fact that at the Annual Meeting of the Institute last May he was awarded the Bessemer Gold Medal.¹ I shall not refer again to his many qualifications to receive that honour, but I would assure him that we congratulate him most heartily and wish him long life and health to enjoy it. (*Applause.*)

Mr. J. H. WHITELEY, in reply, said : I want in the first place to apologise for my absence from the last Meeting of the Institute. If I had had any inkling of what was coming I would certainly have made a strenuous effort to be present. It never occurred to me that the work I had done would ever be considered of sufficient value to merit the Bessemer Gold Medal. The award has exceeded the height of my ambition. On many occasions in the past I have listened to the responses of the recipients of that honour and always with the comfortable feeling that such an ordeal would never be mine. Anyway, I think it will not be without precedent if I take the opportunity of mentioning one or two incidents in my life.

At the age of fifteen, family circumstances made it necessary that I should seek employment, although I would much rather have remained at school, for I then had no leanings towards any particular occupation. After making one or two enquiries, an influential official in a large steel company told me of a vacancy in the drawing office, and wished me to apply for the post, which I did. Now, the way through the works to the required interview went by the laboratory, and it so happened that just as I got there a youth walked out with a large funnel in his hand containing a precipitate which he threw on a scrap heap. That was, of course, a very trivial incident, but nevertheless it determined my career, for, during the interview, the question was put to me as to what I would like to be, and with that young man still in mind I imme-

¹ See *Journal of The Iron and Steel Institute*, 1943, No. I., p. 3 P.

diately said "a chemist." The consequence was that I failed to obtain the situation. However, some few weeks later I heard of another opening in a steelworks, this time in the laboratory. I accordingly made application, and, after an interview with the manager, was accepted. I feel very thankful to-day that during that interview the same question was not again put to me, for, in the vacillating state of mind in which I was, it is quite likely that I would have said "a draughtsman!"

On making a start, almost the first thing I heard was that the manager considered a laboratory in a steelworks to be a necessary evil, and even now I am not quite sure whether that attitude of mind in the industry has entirely vanished. I soon became very disappointed with the work, for I found that my chief duties were the sampling and subsequent preparation of materials such as pig iron, ores, &c., and that continued uninterruptedly for seven long years. I am not bemoaning it, for there could be no doubt that the exercise did me good, but I have ever since regretted the loss, as regards my scholastic development, of those valuable years.

By the time I was twenty-two, matters looked pretty hopeless; so much so that I was on the point of finding another occupation when a change occurred and I was made assistant to Mr. Arthur Braithwaite, the first of three gentlemen whose names I would like to connect with the award. An unassuming but very competent chemist, Mr. Braithwaite laid the foundation during the two years that I was under him for whatever work I have since done. The next gentleman whom I wish to mention is the late Dr. J. E. Stead of very pleasant memory. His friendly encouragement and inspiring example have influenced me all my life. The third gentleman who gave me great assistance was Dr. A. F. Hallimond. I understand that the President, in announcing the award at the last Meeting, referred to a paper on the acid hearth and slag of which Dr. Hallimond and I were the joint authors, and I would now say that whatever excellence that paper may have, at least one half of it is due to Dr. Hallimond. We worked together for about four years during the last war, and that association has been of incalculable benefit to me.

In conclusion I would ask the President and Members of Council to accept my most sincere thanks for the great honour they have conferred on me. (*Applause.*)

BALLOT FOR THE ELECTION OF NEW MEMBERS AND ASSOCIATES.

Dr. DAVID BINNIE (Irlam, near Manchester) and Mr. N. D. RIDSDALE (Middlesbrough) were appointed scrutineers of the ballot for the election of new Members and Associates, and reported that the following one hundred and twenty Members and sixty-one Associates had been elected :

MEMBERS.

ARORA, SATYA PAUL, F.Sc. (Punjab University)	Jamshedpur, India.
ASH, FRANK SEYMOUR	Rotherham.
BARRITT, RICHARD J., M.A., A.M.I.Chem.E.	Cheadle Heath, Stockport.
BEESTON, JOSEPH WILLIAM ULICK	Kettering, Northants.
BEIGHTON, REUBEN	Rawmarsh, Rotherham.
BEVAN, TREVOR	Shotton, Chester.
BINGHAM, REGINALD HARRY, M.I.M.E.	Redbourn, Herts.
BONNEY, <i>Sergeant</i> HARRY FREDERIC	Liancadle, Barry, Glam.
BOOTH, JOHN, B.Sc.	Rawmarsh, Rotherham.
BOROWIK, <i>Major</i> ALBERT	London.
BROCKLESBY, GEORGE EDWARD CECIL	Parkgate, Rotherham.
BROWN, WILLIAM EDWARD LEIGHTON	Shepreth, Herts.
BRYSON, JAMES BALLANTYNE	Mossend, Lanarkshire.
BURLEY, VICTOR GEORGE, A.M.I.Mech.E.	London.
BURNS, JOHN NORMAN, B.Sc., M.I.Mech.E.	Karabuk, Turkey.
CAMERON, JOHN, B.Sc., Ph.D., A.I.C.	Glasgow.
CAMM, JOHN CHARLES	Parkgate, Rotherham.
CAMPBELL, JOHN	Corby, Northants.
CONROY, GEORGE HARRY	Birmingham.
CROSSLEY, DOUGLAS WILLIAM, B.Met. (Sheffield)	Sidecup, Kent.
DOXEY, GERARD, M.Sc.(Tech.)	Corby, Northants.
FINLAYSON, THOMAS CAMPBELL, B.Sc. (Hons. Met.), M.Sc.(Manchester)	Guildford, Surrey.
FULLMAN, BENJAMIN, B.Sc.(Lond.), A.I.C.	Berkhamsted, Herts.
GILL, ANTHONY CHARLES	Stockton-on-Tees.
GILPIN, W., B.Sc., A.R.C.S., D.I.C., Ph.D.	Hartlepool.
GLENDENNING, CHARLES	Queensferry, Chester.
GOLDSCHMIDT, HELMUT JULIUS, M.Sc. (Physics) (Manchester)	Sheffield.
GOUGH, GEORGE HENRY	Parkgate, Rotherham.
GRANT, JAMES	Mossend, Lanarkshire.
GRASSIE, ROBERT G.	Connah's Quay, Chester.
GRAY, BASIL	Sheffield.
GROOM, EDWARD JAMES	Flitwick, Beds.
HAINES, ERNEST	Rawmarsh, Rotherham.
HARRISON, JOHN LAWRENCE	Scunthorpe, Lincs.
HAYWARD, OWEN CHAMPNESS	Rawmarsh, Rotherham.
HERZIG, ALVIN JOHN	Detroit, Mich., U.S.A.
HILLIARD, JOHN O.	Karabuk, Turkey.
HOLLOWOOD, JOHN	Queensferry, Chester.
HORSFIELD, WILLIAM VICTOR	Penistone, Sheffield.
HUNT, LESLIE BERNARD, M.Sc., Ph.D., A.R.C.S.	London.
HURD, HAROLD	Greasbro', Rotherham.
ILLINGWORTH, JACK	Farnley, Leeds.

JONES, KENNETH BRUNTON, Assoc.Met. (Sheffield)	Corby, Northants.
JONES, NOEL WYCHE	Mold, Flintshire.
LABAN, NORMAN ROSCOE, B.Sc.(Hons.) (Birmingham), A.I.C.	Burnham-on-Sea, Somerset.
LAWLEY-WAKELIN, DAVID WILLIAM	Sheldon, Birmingham.
LEADBEATER, ALBERT WILLIAM, A.M.C.T., A.M.I.E.E.	Corby, Northants.
LEWIS, CLARENCE	Shotton, Chester.
LUNT, ALFRED PARKS	Rotherham.
MACDOUGALL, MATTHEW	Corby, Northants.
MACGREGOR, KENNETH, A.M.I.Chem.E., A.M.I.GasE.	Cheadle Heath, Stockport.
MACINTYRE, GEORGE RUSSELL	Newcastle-on-Tyne.
MACLACHLAN, GEORGE	Glasgow.
MAGUIRE, ALEXANDER BAXTER	Sheffield.
MARTIN, FREDERICK CHARLES, B.Sc. (Met.)	Totley, Sheffield.
MAULIK, SUSHIL CHANDRA GUHA	Jamshedpur, India.
MAXWELL, Dr. HAROLD L.	Wilmington, Delaware, U.S.A.
MELTHAM, GEORGE HENRY	Old Brumby, Lincs.
MILLINGTON, GEORGE	Shotton, Chester.
MISRA, DEVA DHAR, B.Sc.(Met.)	Lucknow, India.
MITTER, BAIDYANATH	Jamshedpur, India.
MOORE, DONALD CLAGUE	Portsmouth.
MORGAN, EDWIN, M.Sc.(Met.)	Wollaton, Notts.
MORRIS, ARTHUR NEVILLE	Corby, Northants.
MOSELEY, BERNARD ROBERT	Manchester.
NICOL, JAMES	Mossend, Lanarkshire.
NORTH, J. D.	Wolverhampton.
OXBY, GEORGE ALFRED, B.Met.(Sheffield)	Sidcup, Kent.
PAGETT, ERNEST, A.M.I.Mech.E.	Dudley.
PARNHAM, HAROLD	Workshop.
PARRY, HERBERT	Connah's Quay, Chester.
PATERSON, DAVID RALSTON	Motherwell, Lanarkshire.
PEPPER, HORACE RODWELL	Corby, Northants.
PICKUP, LEWELYN, M.Sc.(Lond.), Ph.D.(Wales)	ShIPLEY, Yorks.
PINOFF, F. M.	Gidea Park, Essex.
PONTER, FRANK WOODFIELD	Corby, Northants.
RAIT, JOHN RHYNAS, B.Sc.(Hons.), Ph.D., A.R.T.C.	Sheffield.
RAJAGOPALAN, SESHADRI, B.Sc.(Met.)	Calcutta, India.
REBER, JAMES WILSON	Cheam, Surrey.
REED, CHARLES ALBERT	Saltburn-by-the-Sea.
REID, CYRIL, B.Sc., Ph.D., A.R.C.S., D.I.C.	Hartlepool.
RIDER, DOUGLAS, O.B.E.	Guildford, Surrey.
ROBINSON, FRANK	Sheffield.
ROLLASON, MELVYN H.	Stoke-on-Trent.
SAIN-MILETITCH, BRANKO, B.Sc.(Belgrade)	Barnet, Herts.

SAUNDERS, ERNEST GEOFFREY, M.A. (Cantab.)	Weekley, Northants.
SCOTT, GEORGE ARTHUR	London.
SHARP, CHARLES ALFORD	Kettering, Northants.
SHUKER, ALBERT EDWARD	Chester.
SMITH, HARRY	Risley, Derby.
SMITH, MATTHEW B.	Newcastle-on-Tyne.
SMITH, STANLEY HICKMAN, B.Sc. (Hons. Met.)	Davenham, Cheshire.
SMITH, STANLEY JAMES WILLIAM	Corby, Northants.
STEWARDSON, HAROLD	Footscray, Victoria, Aus- tralia.
SUMMERSON, THOMAS HAWKSLEY	Darlington.
SUNDARAM, C. K., B.A.(Madras)	Jamshedpur, India.
SWIFT, JOHN THOMAS	Rotherham.
TAYLOR, ANDREW WILFRID	Ishapore, India.
TAYLOR, RICHARD GEORGE HOWE	Knutsford, Cheshire.
THORNTON, BEN	London.
THROSSELL, STANLEY GORDON	Manchester.
TORRANCE, SYDNEY, B.Sc., Ph.D., A.R.C.S., D.I.C.	London.
TORRY, ALAN	Sheffield.
TOWNSEND, JOHN DENNIS	Bramcote, Notts.
TUBBS, WILLIAM HENRY, M.Sc.(Eng.)	Saltburn-by-the-Sea.
VENKITRA RAMAN, P. G., B.Sc. (Madras)	Jamshedpur, India.
WAGSTAFF, JAMES BUCHANAN, B.Sc. (Sheffield)	Sheffield.
WALKER, WILLIAM DUNLOP, B.Sc., A.R.T.C.	Hamilton, Lanarkshire.
WALKLATE, EDWARD JAMES	Stanion, Northants.
WATSON, THOMAS	Sheffield.
WATTS, BRIAN GEORGE, B.Sc., A.I.C., A.I.Mech.E.	Rosario, Argentina.
WEBSTER, HAROLD	Old Brumby, Lincs.
WEIR, STANLEY	Connah's Quay, Chester.
WESTWOOD, HORACE VICTOR	Walsall, Staffs.
WHITE, BERNARD FEARN	Rotherham.
WILLIAMS, JOHN EDWARD, B.Sc. (Hons. Met.)	Llanelly, Carmarthenshire.
WILLMOTT, WILFRID ERIC, B.Sc., A.I.C.	Bristol.
WOOD, JOHN HAROLD	Kimberworth, Rother- ham.
WRIGHT, KENNETH HUGH	West Bromwich.
YUILL, GEORGE COMRIE	Larbert, Stirling.

ASSOCIATES.

ABRAMS, S. M., B.Sc.(Eng.)	Springs, Transvaal, South Africa.
ADAIR, JAMES ROY	Mossend, Lanarkshire.
BALAJIVA, KASEM	Sheffield.
BALDWIN, EDWIN HORACE	Glasgow.
BALL, JOHN GEOFFREY	Purley, Surrey.

BARBER, GEORGE	Newcastle-on-Tyne.
BODSWORTH, C.	Sheffield.
BRUNTON, <i>Miss</i> MARY	Wishaw, Lanarkshire.
BURDEN, WALTER HENRY ALDWYN	Wolverhampton.
BUSBY, ARTHUR DONALD	Erdington, Birmingham.
CARTER, PERCIVAL THOMAS	Glasgow.
COURTNEY, JAMES McMILLAN	Hamilton, Lanarkshire.
DAVIES, DAVID ROBSON GLYN	Builth Wells, Breconshire.
DAVIES, JOHN ELVET	Gowerton, Swansea.
DUFFY, EMILE JAMES	Coatbridge, Lanarkshire.
ELDRIDGE, GEORGE WILLIAM	Distington, Cumberland.
ESNAWY, ADLY HASSAN, B.Sc.(Met.).	London.
EVANS, EDWARD JAMES	Gorseinon, Glam.
EVANS, JOHN OTHNIEL	Pontardawe, Swansea.
FISHER, JOSEPH GRANT	Bellshill, Lanarkshire.
FRASER, ALEXANDER, B.Sc., A.R.T.C.	Corby, Northants.
GEORGE, IDRIS	Kenfig Hill, Glam.
GILCHRIST, JAMES DUNCAN, B.Sc., A.R.T.C., A.I.C.	Glasgow.
GILMOUR, THOMAS	Shotts, Lanarkshire.
GLEDHILL, PHILIP KNOWLES	Honley, Huddersfield.
GREEN, WILLIAM ERNEST	Codsall, Wolverhampton.
GRIFFITHS, PETER	Gorseinon, Glam.
GRIMSHAW, WILLIAM HENRY	Bellshill, Lanarkshire.
HARRIS, FRANCIS WALTER BRIAN	Woldingham, Surrey.
HAWKE, RONALD STEWART	London.
HOSKISSON, <i>Miss</i> MARGARET	Derby.
HUGGINS, LEONARD JOHN	Loughborough.
JONES, DAVID JENKINS	Pontardawe, Swansea.
JONES, GLANVILLE	Llangain, Carmarthen.
KERR, CECIL PATERSON	Cleland, Lanarkshire.
KINGSTON, RONALD	Middlesbrough.
LEWIS, DESMOND	Ash, Surrey.
McCULLOCH, GEORGE CARLAW	Wishaw, Lanarkshire.
MCLEOD, JOHN MITCHELL	Paisley.
MILNE, MAURICE	Aberdeen.
MOORE, WILLIAM JACKSON MILES, B.Sc.(Met.)	Littleover, Derby.
MORGAN, BRINLEY	Ystalyfera, Swansea.
MURRAY, PETER WOOD	Motherwell, Lanarkshire.
NAISMITH, JOHN ANDREW	Hamilton, Lanarkshire.
OWEN-BARNETT, RICHARD ARTHUR	Sully, Glam.
PARGHI, HERENDRA S.	Patan, Baroda State, India.
PURCELL, WILLIAM JOHNSTON	Jerviston, Lanarkshire.
QUICK, HAROLD LLEWELLYN	Coventry.
RAHAKANTHAN, M., B.A.	Benares, India.
ROBERTS, ERIC WILLIAM	Hawthorn, Wilts.
ROBERTS, JAMES AUBREY	Wednesbury, Staffs.
ROBINSON, PETER JAMES	Sheffield.
SAVAGE, THOMAS RAYMOND	Hendon, Sunderland.
SHIELDS, REGINALD HAMILTON LLEWELLYN	Bangor, N. Ireland.
SKERRY, ERNEST WILLIAM, B.Sc. (Hons.)	Warrington.

TAYLOR, PERCY RONALD	Woodhouse, Sheffield.
WARREN, BRYAN RALPH	London.
WATTS, GEORGE ROLAND	Alsager, Stoke-on-Trent.
WEIMER, D. E. H.	London.
WEIR, JAMES	Bellshill, Lanarkshire.
WILSON, KEITH ROWLEY	Horfield, Bristol.

ANDREW CARNEGIE RESEARCH GRANT.

The SECRETARY announced that the following Andrew Carnegie Scholarship grant had been awarded by the Council :

M. S. WANG (Sheffield University)—£150 to assist in a research on the effect of repeated heat treatment on steels.

Complete List of Papers Presented at the Autumn Meeting in London, 1943.

"Fourth Report of the Oxygen Sub-Committee." (Paper No. 22/1943 of the Committee on the Heterogeneity of Steel Ingots.)

A. J. COOK and F. W. JONES : "The Brittle Constituent of the Iron-Chromium System (Sigma Phase). I.—A Survey of the Limits of the Sigma Phase in the Binary System." (Paper No. 11/1943 of the Alloy Steels Research Committee.)

W. DAVIES and W. J. REES : "British Resources of Steel Moulding Sands." (Paper No. 4/1943 of the Steel Castings Research Committee (submitted by the Moulding Materials Sub-Committee).)

J. C. HUDSON : "Present Position of the Corrosion Committee's Field Tests on Atmospheric Corrosion (Unpainted Specimens)." (Paper No. 10/1943 of the Corrosion Committee.)

A. JACKSON : "The Maintenance of the Furnace Linings in Large Basic Open-Hearth Tilting Furnaces by the Use of Chrome Ore, Magnesite and Serpentine."

F. LÁSZLÓ : "Tessellated Stresses.—Part II."

E. F. LAW and V. HARBORD : "The Solidification and Cooling of Steel Ingots. Notes on an Examination of Three Typical Ingots." (Paper No. 21/1943 of the Committee on the Heterogeneity of Steel Ingots.)

T. W. PARKER and R. W. NURSE : "Merwinite in the System CaO—MgO—SiO₂."

L. NORTHCOTT and D. MCLEAN : "The Structure and Segregation of Two Ingots of Ingot Iron, One containing Lead."

T. H. SCHOFIELD : "Note on some Precipitation Effects observed in Mild-Steel and Wrought-Iron Pipe."

T. SWINDEN : "Leaded Manganese-Molybdenum Steel." (Paper No. 13/1943 of the Alloy Steels Research Committee).

F. V. WARNOCK and J. B. BRENNAN : "Some Tensile Shock Properties of Carbon Steels."

J. WHITE : "The Physical Chemistry of Open-Hearth Slags."

J. H. WHITELEY : "A Study of Austenitic Grain Growth in Medium-Carbon Steels." (Paper No. 12/1943 of the Alloy Steels Research Committee.)

PRESENTATION OF PAPERS.

A list of the papers included in the programme of the Meeting will be found on p. 9 P. The following were presented for verbal discussion :

Morning Session.

"A Study of Austenitic Grain Growth in Medium-Carbon Steels." By J. H. WHITELEY.

"The Structure and Segregation of Two Ingots of Ingot Iron, One containing Lead." By L. NORTHCOTT and D. MCLEAN.

"Leaded Manganese-Molybdenum Steel." By T. SWINDEN.

The last two papers were discussed jointly.

Afternoon Session.

"The Solidification and Cooling of Steel Ingots. Notes on an Examination of Three Typical Ingots." By E. F. LAW and V. HARBORD.

"The Physical Chemistry of Open-Hearth Slags." By J. WHITE.

BRITISH RESOURCES OF STEEL MOULDING SANDS.

By W. DAVIES, M.Sc., F.G.S., AND W. J. REES, D.Sc.TECH., F.I.C.
(UNIVERSITY OF SHEFFIELD).

(Figs. 13 to 34 = Plates I. to IV.)
(Figs. 39 to 46 = Plates V. and VI.)
(Figs. 51 to 62 = Plates VII. and VIII.)
(Figs. 65 to 69 = Plate IX.)

*Paper No. 4/1943 of the Steel Castings Research Committee
(submitted by the Moulding Materials Sub-Committee).*

PART 1.—THE UPPER CARBONIFEROUS GRITS AND SANDSTONES OF THE EASTERN PART OF THE PEAK DISTRICT.¹

(Figs. 13 to 34 = Plates I. to IV.)

SUMMARY.

In the First Report of the Moulding Materials Sub-Committee (Third Report of the Steel Castings Research Committee), pp. 191–200, attention was directed to the characteristics of certain crushed grits. In view of the possible usefulness of several of the grits examined then for the preparation of moulding materials for the steel foundry, it was considered desirable to make a more complete investigation of the grits and sandstones accessible to steelmaking districts. The present Part deals with the Upper Carboniferous grits and sandstones of the Peak District, which is within easy reach of Sheffield, Lancashire and the Midlands; in subsequent Parts the grits, &c., of other areas are dealt with.

Attention is directed to the relationship between the petrology and the moulding characteristics of grits, and it is shown that from a petrological examination to determine the mineralogical composition (by micrometric analysis) and the microstructure, useful indications can be obtained of the form of the mechanical-grading curve, the green strength and permeability, and the refractoriness.

The important petrological features of the type of grit likely to be suitable for steel-moulding purposes are :

- (a) The grain size should be uniform (0.3–1.0 mm.).
- (b) Sintering in the quartzitic aggregates should be simple, so that the proportion of composite grains in the crushed material will be small. It also appears to be desirable that the quartz grains should be free from strain.
- (c) The quartz content should be not less than 80%.
- (d) The content of sericite and kaolin should not be high, because of their effect in increasing sinterability; the presence of some limonite is advantageous, but its proportion should not be high. A feldspar content as high as 10% may not be detrimental if it is fresh, although a high feldspar content reduces the ultimate refractoriness of the crushed grit.

¹ Received February 25, 1941. This paper is published by authority of the Steel Castings Research Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

Certain of the crushed grits have characteristics similar to those of synthetic moulding materials, based on high-silica sands, at present used in steel foundries.

I.—INTRODUCTION.

PUBLISHED information on the use of Upper Carboniferous rocks for moulding purposes is scanty. The results of laboratory tests on several grits from Derbyshire were described by K. W. Slack and W. J. Rees ¹ two years ago. As described by P. G. H. Bos-

TABLE I.—*Index to the Rock Samples.*

Ref. No.	Geological Horizon.	Locality.
S1	Crawshaw Sandstone.	Middlewood Quarry, near Sheffield.
S2	Kinderscout Grit.	Leam Quarry, near Hathersage.
S3	Upper Burbage Grit.	Surprise Quarry, near Hathersage.
S3W	Upper Burbage Grit (weathered).	Surprise Quarry, near Hathersage.
S4	Rivelin Grit.	Bell Hagg Quarry, near Sheffield.
S5	Upper Burbage Grit.	Houndkirk Quarry, near Ringinglow.
S6	Brown Edge Flags.	Brown Edge Quarry, near Ringinglow.
S7	Upper Burbage Grit.	"Clarion" Quarry, near Ringinglow.
S8	Kinderscout Grit.	Stoke Quarry, near Grindleford.
S9	Upper Burbage Grit.	Longshaw Quarry, near Grindleford.
S10	} Kinderscout Grit.	Birchover, near Bakewell.
S11		
S12		
S13	Kinderscout Grit.	Stancliffe Quarry, Darley Dale.
S14	Kinderscout Grit.	Black Rocks Scree, near Cromford.
S15	Kinderscout Grit.	Shire Hill Quarry, near Glossop.
S16	Kinderscout Grit.	Ladybower Quarry, near Ashopton, west of Sheffield.
S17	Rough Rock.	Alton Quarry, near Clay Cross.
S18	Rivelin Grit.	Rivelin Edge, Lodge Moor, near Sheffield.
S19	Chatsworth Grit.	Beeley Moor, near Rowsley.
S20	Wingfield Flags.	Bolehill Quarry, west of Chesterfield.
S21	Rough Rock.	Red Lion Inn, near Chesterfield.
S22	Chatsworth Grit.	Roaches Quarry, west of Chesterfield.
S23	Wingfield Flags.	Freebirch Quarry, west of Chesterfield.
S24	Grenoside Rock.	Wortley Stone Quarries.
S25	Greenmoor Rock.	Greenmoor Quarry, near Stocksbridge.
S26	Rough Rock.	Hazlehead.
S27	Huddersfield White Rock.	Langsett Moors.
S28	Rivelin Grit.	Rivelin Glen Quarry, Malin Bridge, near Sheffield.
S29	Rivelin Grit.	Disused Quarry, west of Malin Bridge, near Sheffield.
S30	Loxley Edge Rock.	Disused Quarry, east of Bolsterstone.

¹ First Report of the Moulding Materials Sub-Committee, Third Report of the Steel Castings Research Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 23*, p. 191 *et seq.*

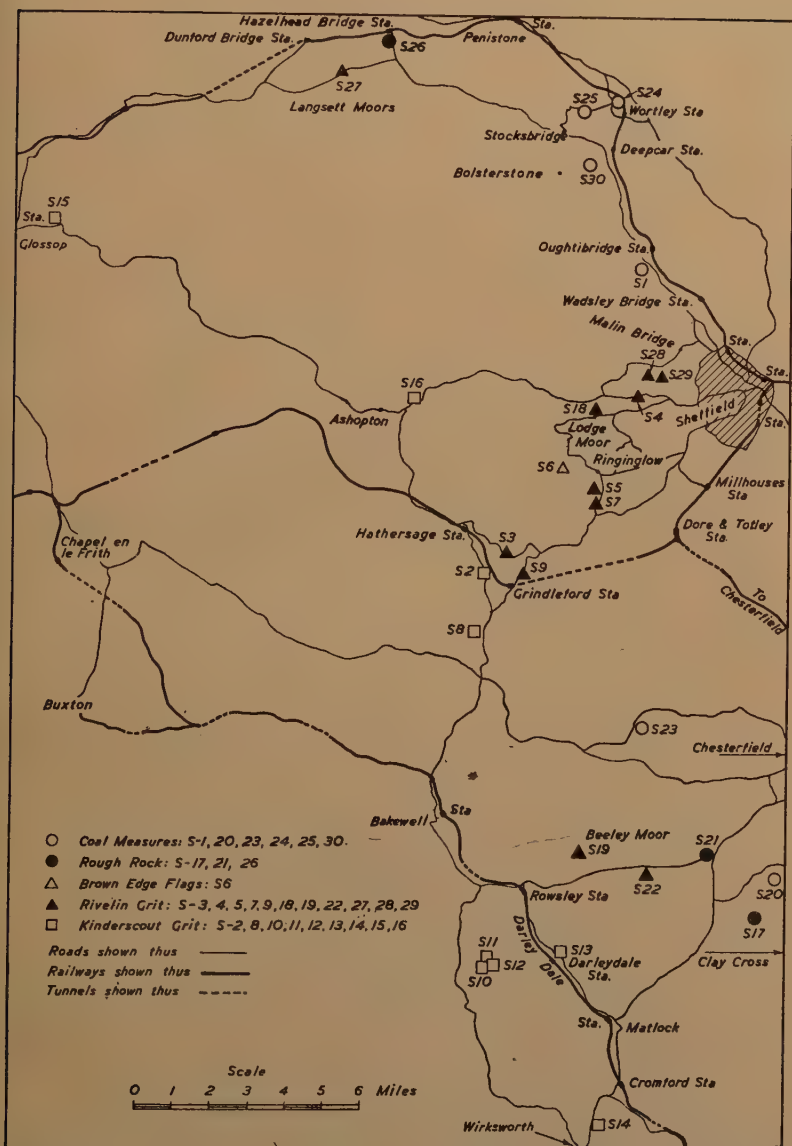


FIG. 1.—Localities from which the Rock Samples were obtained. The numbers refer to the Index in Table I.

well,¹ the "rotten rocks" and "rotten stone" of Glasgow and the Lowland Valley of Scotland are used in the local steelmaking industry.

The use of the Peak District grits for moulding is only just beginning. One firm of moulding sand producers has had several loads of weathered grit from the Houndkirk Quarry, near Ringinglow, for experimental work (*see sample S5*²). Another producer is supplying one foundry with a mixture of crushed grit and fire-clay (*see sample S22*). Several steel foundries are using crushed grit from the Biddulph sandstone.

In this paper, emphasis is laid on the relation of the moulding properties to the geological characters of the grits. This involves certain assumptions, which are mentioned later, concerning the nature of the ideal moulding sand.

The rocks examined are felspathic grits and sandstones. They are composed essentially of quartz and a variable proportion of felspar, together with some muscovite, sericite, kaolin and limonite. It was found that the quartz content of the crushed grits could be increased considerably by sieving and washing.

An index to the rock samples is given in Table I. The localities are shown on the map, Fig. 1.

II.—STRATIGRAPHICAL DISTRIBUTION.

A generalised north-south section of the grits on the eastern side of the Peak District is shown in Fig. 2. On it are marked the approximate positions of the localities from which the samples were obtained.

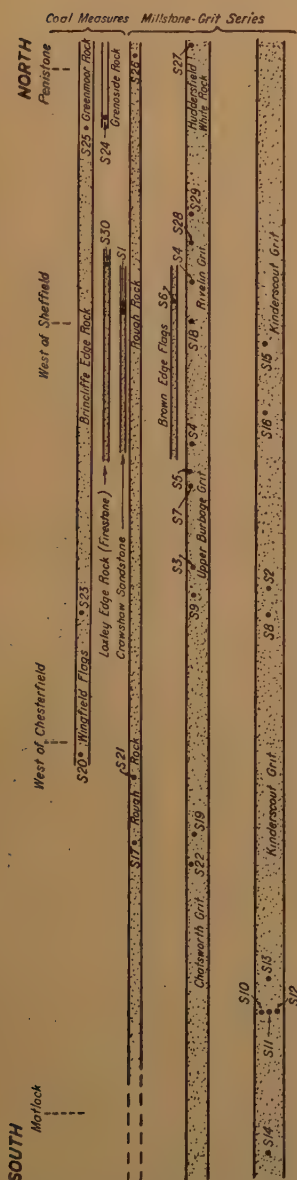
The moulding properties of the crushed grits do not depend so much on their geological horizons as on the geological character of the grit at the locality concerned. It is possible, however, to make certain generalisations.³ The Kinderscout, or Fourth, Grit is usually coarse-grained around Ashover. Near Chatsworth this grit is fine-grained, but between Bamford and Penistone it is very coarse and often pebbly. The Rivelin, or Third, Grit is coarse-grained round Ashover, but becomes fine-grained and almost silty on Beeley Moor, near Chatsworth. Further north on Froggatt, Burbage and Rivelin Edges, it becomes coarse-grained once more and finally disappears around Midhopestones. The Second Grit is a series of grit lenses of very variable character. The Rough Rock, or First, Grit, is very uniform over the whole area; it is a medium- to coarse-grained grit. As a rule, the Coal Measure grits or sandstones are not so coarse-grained as the Millstone Grits.

The character of the grit may change within the limits of one

¹ "A Memoir on British Resources of Refractory Sands," p. 116. London, 1918: Taylor and Francis.

² See detailed descriptions in Appendix A.

³ A. H. Green and others, "The Geology of the Yorkshire Coalfield," p. 27 *et seq.* *Memoirs of the Geological Survey of Great Britain*, 1878.



quarry face. This variation is conspicuous in the Rivelin Grit of Bell Hagg Quarry (S4). As will be seen from the generalised section, Fig. 3, the rock changes from a band of pebbly grit or

conglomerate through coarse-grained grit to fine-grained grit between one major bedding plane and the next. At the top of the face, only fine-grained, flaggy sandstone is to be found.

III.—PETROLOGY.

The rocks examined range from quartzites, through grits and sandstones, to siltstones. Many of the grits are so felspathic that they may well be called "arkoses." In brief, the rocks are the reconsolidated débris of disintegrated acid igneous and metamorphic rocks, a conclusion due to H. C. Sorby¹ and amplified by A. Gilligan.² Accordingly the rocks are composed mainly of quartz, feldspar, mica, kaolin, limonite and calcite. Besides these dominant minerals, there is a small proportion of heavy minerals, chiefly zircon, rutile, tourmaline, garnet, magnetite, ilmenite and leucoxene. As will be seen from the following descriptions, the habit of each mineral depends on its origin, on the grain size of the rock of which it is a constituent and on the changes it has undergone prior to, and during, consolidation.

Detailed descriptions of the petrology of the samples will be found in Appendix A.

Dominant Minerals.

Quartz.—This mineral was derived from such rocks as granite, granite-gneiss, siliceous schists and metamorphic quartzites. Most of it was deposited on the Upper Carboniferous sea-floor as single grains, though some was deposited as small rounded quartzite pebbles and as composite grains.

Many of the single grains were derived from rocks which had been subject to regional metamorphism. Consequently they show the effects of shearing, either as permanent strain indicated by shadows when the microsection is examined under crossed nicols, or by slip-planes the traces of which are indicated in the section by lines of bubbles. Fig. 13 is a micrograph of a quartz grain containing more or less parallel lines of bubbles. As will be seen from



FIG. 4.—Bubble Inclusions in Strained Quartz Grains.

the sketches in Fig. 4, the bubbles may be arranged in intersecting lines or in roughly parallel lines.

Some of the single grains were derived from unsheared rocks,

¹ *Proceedings of the Yorkshire Geological Society*, 1859, vol. 3, pp. 673-674.

² *Quarterly Journal of the Geological Society*, 1919, vol. 75, pp. 251-294.

as, for instance, many granites. Such grains are rarely strained, and the bubble inclusions have no linear pattern.

Graphs, such as those given by Boswell (*loc. cit.*), show that the bulk of a satisfactory moulding sand consists of grains 0.5–0.25 mm. across. Since quartz has no cleavage, the shape of the quartz grains in this fraction of the crushed rock is closely related to the pattern of the bubble inclusions and to the size of the grains in the uncrushed rock.

For instance, the quartz grains in the Chatsworth Grit of Beeley Moor (S19) are fairly uniform in size and 0.25–0.30 mm. across. Some of them enclose linearly-arranged bubbles—that is, the grains are strained—but in the majority the bubbles are scattered irregularly—that is, the grains are unstrained. During crushing, the strained grains break along the slip-planes into particles less than 0.25 mm. across and therefore disappear from the fraction in question. The unstrained grains are much more resistant to crushing and, unless the pressure is great, only the angular corners spall away, thus leaving more-rounded though slightly smaller grains. If the pressure is great enough, the unstrained grains break conchoidally into angular fragments less than 0.25 mm. across and disappear from the fraction. Consequently the quartz grains in this fraction of the crushed rock are mainly subangular-to-rounded in form.

Very different is the case of the Rivelin Grit from Bell Hagg (S4). The uncrushed grit is composed mainly of large grains up to 0.7 mm. or more across, more or less strained and containing bubble inclusions. The quartz grains in the 0.5–0.25-mm. fraction vary in shape (*see* Fig. 24). Some of them are angular and were formed by the conchoidal fracture of large, single grains in which the bubble inclusions were arranged at random. Less angular grains were formed by the fracture of the large strained grains along the slip-planes. Subangular-to-rounded grains were formed from unstrained grains, about 0.5 mm. or less across in the uncrushed grit, by the spalling of the corners.

This variation in shape is best developed when a jaw-crusher is employed. If an edge-runner mill is used, the corners of the more angular grains tend to spall off, so that more of the quartz grains are subangular in shape.

The pattern of the slip-planes in the strained quartz grains varies too much from grain to grain in the same rock for any conclusions to be drawn concerning the effect of different patterns on the shape of the crushed grains. The proportion of strained grains varies from locality to locality. The quartz grains in the siltstones, being smaller than those of the other rocks, rarely contain linearly arranged bubbles.

It can be shown that many of the single grains were subangular or even rounded prior to the consolidation of the sediment. During consolidation, silica was deposited on the original grain in optical

continuity. In many grains, the boundary between this layer of secondary quartz and the original grain can be distinguished by a layer of air bubbles trapped in the junction. Fig. 14 is a micrograph of a quartz grain in which the boundary of the original rounded grain can be distinguished by a faint line of bubbles (indicated by arrows) close to the margin of the grain. As crossed nicols were used, the present boundary of the grain against the adjacent darker grains can be seen. This layer of quartz is thin where the grains were originally in contact and thick where pores formerly existed. Sketches of other grains with layers of secondary quartz are shown in Fig. 5. Secondary silicification usually increases the angularity of a grain.

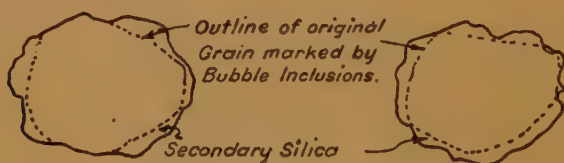


FIG. 5.—Secondary Silicification of Quartz Grains.

In the rocks examined, the outline of the original grain is indicated usually by trapped air bubbles. Occasionally, it is marked by limonitic or clayey matter adhering to the surface of the original grain. If, as sometimes happens, crushing does not remove the secondary silica shell, this limonitic or clayey matter will reduce the refractoriness and resistance to sintering without improving the bond strength. This point is of more importance in the Trias sandstones, such as the Penrith Sandstone, than in the Upper Carboniferous rocks.

Though some of the secondary silica which encloses the quartz grains may have been derived from the decomposition of unstable silicates such as felspar, much of it was dissolved from the quartz grains themselves. During the consolidation of the rock, secondary silicification often occurs on an extensive scale and, as a result, quartz grains in parts of the rock are cemented together by secondary silica until they are quartzites. These patches of silica-cemented quartz grains appear as "quartzitic aggregates"¹ in the micro-sections (see Figs. 24 to 31). They are formed by the solution of silica at the points of contact between the grains due to local pressure, and by the deposition of silica in optical continuity on the grains where they are not in contact, as indicated in Fig. 6(a). In this way the grains become more and more tightly packed together until, finally, the interstices are completely filled. The new boundaries of the grains vary considerably; they may be

¹ H. M. Hudspeth and D. W. Phillips, "Coal Measure Rocks," *Safety in Mines Research Board*, 1937, *Paper No. 98*, p. 7, refer to these patches as "quartzitic areas."

simple with little or no interlocking, as in Fig. 6(b), or they may be so intricately sutured together that the boundaries are a series of dovetailed joints, as in Fig. 6(c).

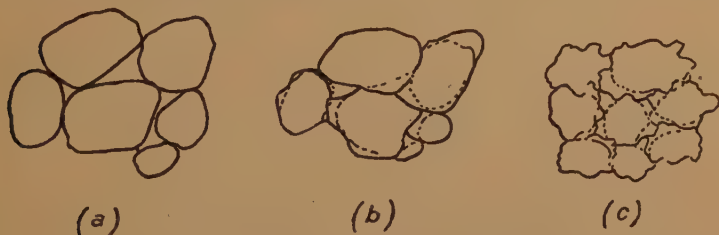


FIG. 6.—The Formation of Quartzitic Aggregates.

During crushing, these types of quartzitic aggregates behave differently. If the boundaries are simple, the grains separate from each other and are subangular in shape, as in Fig. 7(a). The crushing of the grains themselves will produce the shapes already described for single grains. If the boundaries are dovetailed, the grains fracture conchoidally or along slip-planes rather than along the boundaries, and the resulting composite grains will be angular, as in Fig. 7(b). When fracture does occur along the boundaries, as in Fig. 7(c),

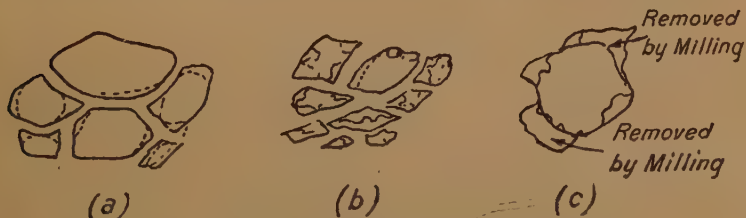


FIG. 7.—The Crushing of Quartzitic Aggregates.

the dovetail suturing is broken and the resultant grains are composite. If these composite grains are free from slip-planes, further crushing will remove the corners and some of the included dovetail fragments of other grains, as in Fig. 7(c).

The conglomerate bands and some of the coarse grits contain quartzite pebbles and composite grains derived from quartzites of metamorphic origin. During crushing, these quartzite pebbles and composite grains behave in the same way as the quartzitic aggregates just described.

The roughness of the surfaces of the quartz grains in the crushed grit depends on the mode of formation of the crushed grains. Grains formed by conchoidal fracturing have smooth, curved or slightly corrugated surfaces, to which the bond will not adhere readily. Milling abrades these surfaces and provides a good key

for the bond. Grains produced by fracture along slip-planes have pitted surfaces due to the air bubbles trapped in the slip-planes. The third type of grain, which has been rounded by the spalling of the corners, usually has an abraded surface.

Weathering of the quartz grains does not, of course, produce any chemical changes. It assists secondary silicification, which shows itself by the development of crystal facets on quartz grains in exposed surfaces. Frost action sometimes causes the quartz grains to part along the slip-planes; this is particularly well shown by the Rough Rock from Hazlehead (S26), see Fig. 15.

Felspar.—Microcline microperthite occurs in most of the rocks, and in some plagioclase is present as well. The grains are nearly all well-rounded or else are fragments of large rounded grains. A typical rounded grain of microcline microperthite is shown in Fig. 16, and one of plagioclase in Fig. 17.

Microcline microperthite is formed by the exsolution of plagioclase from a solid solution of plagioclase in microcline. This exsolution produces the microperthite structure shown in Fig. 18, in which light-coloured wisps of plagioclase are enclosed in a microcline host showing cross-hatching. In some examples the composition of the plagioclase wisps could be determined optically, and in each case it was found to be albite-oligoclase, that is, plagioclase the composition of which is approximately :

90% Albite (Ab), $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$.

10% Anorthite (An), $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

This observation, together with a micrometric analysis, showed that the composition of the microcline microperthite, as a whole, was :

80% Microcline, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$.

20% Albite-oligoclase.

This observation is in accord with those of H. L. Alling.¹

The plagioclase grains vary in composition from andesine to acid labradorite, that is, from $\text{Ab}_{70}\text{An}_{30}$ to $\text{Ab}_{40}\text{An}_{60}$. As a rule, the plagioclase grains are more decomposed than those of microcline microperthite. The felspars of the Millstone Grit are fresher than those of the Coal Measure rocks.

Both types of felspar have two good cleavages, more or less normal to each other. These cleavages are intersected obliquely by two others which are not so well developed. The cleavage traces in a felspar grain are shown in Fig. 19.

When a rock containing felspar is crushed, the felspar breaks readily into small blocks along the cleavages. This process is assisted if the felspar is slightly decomposed, for alteration commences along the cleavage cracks and is accompanied by an increase

¹ "The Mineralogy of the Felspars," *Journal of Geology*, 1921, vol. 29, p. 193.

in volume. The development of sericite along the cleavage cracks is shown in Fig. 20. These blocks are usually less than 0.25 mm. across. As a rule, feldspar crushes more easily than quartz, consequently the 0.5–0.25-mm. fraction of the crushed rock usually contains less feldspar than the original rock. For instance, when a sample of the fresh Upper Burbage Grit from the Surprise Quarry (S3) was crushed, this fraction contained less than 5% of feldspar, although the original rock contained more than 11%. In this way the refractoriness of the crushed grit may be improved.

One of the features of the Millstone Grit of the Peak District is the freshness of the feldspar. The source rocks of the Millstone Grit disintegrated either under glacial, or more probably arid, conditions.¹ Transport to the delta in which the Grit accumulated was rapid, and the rock débris was deposited under conditions which reduced the access of carbon dioxide to a minimum. The rocks of the Coal Measures accumulated in the presence of rather more carbon dioxide.

The least feldspathic of the rocks examined contains 4% of feldspar and many of them contain 10–15%. In this way these rocks differ essentially from the Scottish "rotten rocks." In the latter, the feldspar decomposed into sericite and kaolin, owing to the presence of abundant carbon dioxide while the rock accumulated.

Microcline decomposes slowly under present-day weathering conditions. Grits such as the Rivelin Grit of Lodge Moor (S18, Fig. 21) and the Chatsworth Grit of Beeley Moor (S19), have weathered until they crumble into subsoil of podsol type, and yet the feldspar is almost as fresh as in the unweathered grit. In other words, modern weathering conditions are not severe enough to give to the grits the character of the Scottish "rotten rocks."

The decomposition of feldspar takes place in stages. In the first the feldspar breaks down into sericite (hydro-mica) and colloidal silica, so providing some of the secondary silica attached to the quartz grains. Sericite is a secondary mica, which contains more water than the primary mica muscovite, and in which the alumina may be partly replaced by ferric oxide, derived from the decomposition of ferromagnesian minerals. The decomposition of acid plagioclase, such as albite-oligoclase, yields a little calcite and kaolin as well as sericite and colloidal silica.

In the second stage, sericite decomposes into kaolin together with some limonite and colloidal silica.

The first stage takes place slowly, but the second is comparatively rapid, because of the fine state of division of the sericite. For instance, the weathered Upper Burbage Grit on the tip of the Surprise Quarries (S3W) is stained dark red by the liberated hydrated iron oxide.

Mica.—Three types of mica are present—muscovite; a ferro-

¹ A. Gilligan, "The Millstone Grit of Yorkshire," *Quarterly Journal of the Geological Society*, 1919, vol. 75, p. 287 *et seq.*

magnesian mica related to biotite; and the secondary mica, sericite.

Muscovite flakes occur in most of the rocks, and in some they occur abundantly in layers, imparting a flaggy character to the rock, as, for instance, the Huddersfield White Rock of Langsett Moors (S27). Muscovite flakes are resistant to crushing, for, though they may shear into thinner flakes, these flakes are too large to adhere to the quartz grains and so act as bonding material. During the ramming of the moulding sand around the pattern, such flakes set themselves at right angles to the ramming pressure, and, if they are sufficiently abundant, they will impart a laminated structure to the mould. Furthermore, muscovite lowers the refractoriness and resistance to sintering.

The ferromagnesian mica is pleochroic in shades of brown, and in many cases it is zoned. It is closely allied to biotite and may be biotite from which some of the iron has been leached. It affects the properties of the moulding sand in much the same way as muscovite. Prolonged weathering gradually converts biotite to a secondary mica known as chlorite, and ultimately to kaolin and limonite.

Both biotite and muscovite are primary micas derived by the mechanical disintegration of the source rocks such as granite and mica-schist. Nearly all of the third mica, sericite, was derived by the chemical disintegration of the felspar before the sediment accumulated in the Millstone-Grit delta.

The typical sericite of the grits and sandstones occurs as interstitial aggregates of micaceous wisps. During crushing, these aggregates break up and finely-divided sericite is scattered over the quartz grains, thus forming a good bond for moulding purposes.

The sericite in the siltstones is so abundant that it is not interstitial but envelops the quartz grains and quartzitic aggregates.

In some rocks, the grains in the quartzitic aggregates are coated with a thin film of sericite. This sericite was interstitial to the quartz grains in the unconsolidated sediment, but, as secondary silicification proceeded, it was gradually squeezed between the quartz grains and so formed the thin films observed in the consolidated rock. During crushing, such films assist the quartzitic aggregates to break around rather than across the individual grains. Some of the sericite remains attached to the grains and assists as a bond in the moulding sand.

Kaolin.—Like the sericite, almost all the kaolin was derived by the chemical disintegration of the felspar before the sediment accumulated in the Millstone-Grit delta. The kaolin occurs interstitially as small flakes with vermicular structure. Two kaolin pockets are shown in Figs. 22 and 23. During crushing, the kaolin is scattered over the quartz grains and so acts as a bond in the moulding sand. X-ray examination confirmed that this disintegration product was kaolinite.

Limonite.—This mineral is in most cases closely associated with

the sericite and kaolin. In weathered grit the liberated limonite adheres to the quartz grains, so improving the bond adhesion for moulding purposes. If weathering proceeds to the extreme, as in subsoils of podsol type, the reddish-brown limonite is removed, leaving a grey, crumbly rock.

Calcite.—This mineral is present only in small quantity. It occurs as interstitial patches near to, or as veins in, plagioclase grains.

The proportions of the dominant minerals in the rocks examined are given in Table II. Where less than 1% of a mineral was present it was not determined. The typical size of the quartz grains in the uncrushed rock is also given. Certain of the grits were analysed chemically. In Appendix B these analyses are compared with chemical analyses calculated from the mineralogical analyses given in Table II.

TABLE II.—*Proportions of the Dominant Minerals in the Rocks Examined.*

Rock.	Grain Size. Mm.	Quartz. %.	Felspar. %.	Mica. %.	Kaolin. %.	Limonite. %.	Total. %.
S1	0.5	86.60	9.00	4.43	100.03
S2	0.6	76.40	13.08	8.51	2.00	...	99.99
S3	1.0	79.64	11.02	6.96	2.39	...	100.01
S3W	1.0	63.98	9.52	8.93	← 17.56 →		99.99
S4	0.7	83.30	6.03	6.95	1.12	2.63	100.03
S5	1.0	83.22	7.89	6.98	0.95	1.02	100.06
S6	0.3	85.13	4.19	5.60	...	5.08	100.00
S7	0.8	82.94	4.40	8.63	...	4.02	99.99
S8	1.0	75.98	14.62	7.32	2.06	...	99.98
S9	1.0	86.08	9.12	3.76	1.06	...	100.02
S10	0.5	78.07	11.43	4.13	6.38	...	100.01
S11	0.5	77.82	10.58	4.84	6.76	...	100.00
S12	0.5	79.49	12.86	3.69	3.96	...	100.00
S13	0.5	72.85	15.77	6.54	4.87	...	100.03
S14	0.5	80.24	10.10	4.58	3.42	1.66	100.00
S15	0.8	82.35	9.16	8.23	0.24	...	99.98
S16	0.6	77.67	11.66	9.87	...	0.77	99.97
S17	0.3	82.75	5.16	4.81	7.29	...	100.01
S18	0.5	81.04	9.20	7.58	2.18	...	100.00
S19	0.3	82.08	4.06	8.56	4.25	1.04	99.99
S20	0.1	71.42	6.45	20.28	1.87	...	100.02
S21	0.6	79.84	9.72	6.12	4.31	...	99.99
S22	...	84.35	6.55	6.68	2.44	...	100.02
S23	0.1	69.84	5.99	22.20	2.01	...	100.04
S24	0.4	76.63	10.85	6.13	6.38	...	99.99
S25	0.1	51.52	6.12	← 42.35 →		...	99.99
S26	0.5	75.51	7.34	13.04	4.12	...	100.01
S27a	0.2	73.58	10.35	← 16.10 →		...	100.03
S27b	0.2	81.17	3.25	← 15.59 →		...	100.01
S28	1.5	76.38	14.73	4.99	3.92	...	100.02
S29	1.5	78.11	12.14	4.04	5.68	...	99.97
S30	0.5	92.19	1.33	3.00	3.54	...	100.06

Heavy Minerals.

The proportion of heavy minerals in the crushed rocks varies from 0.05% to 0.15%, that is, the usual proportion found in sands and crushed rocks used for steel moulding.¹ Gilligan (*loc. cit.*) has emphasised that the proportion of heavy minerals varies considerably from bed to bed within the limits of a single quarry. In one quarry he instances garnetiferous layers $\frac{1}{2}$ in. thick which are 500 times as rich in heavy minerals as the normal grit. He showed that the mineral species present vary according to the grain size of the rock, and that the finer-grained the beds are, the greater is the proportion of zircon and rutile in the heavy-mineral assemblage. These conclusions apply equally well to the rocks described in this paper. The species identified in the heavy-mineral assemblages are given in Table III., in which the relative proportions are indicated.

Zircon (ZrSiO_4) occurs as prismatic grains with rounded pyramidal terminations. In some cases it is zoned.

Rutile (TiO_2) occurs either as reddish-brown, well-formed prismatic grains, often with pyramidal terminations, or as yellowish-brown rounded or fractured grains. The prismatic grains are often striated diagonally.

Almandine garnet ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) sometimes occurs as pink rounded grains, but more usually as pink angular fragments due to fracture along the rather indistinct 110 parting.

Tourmaline (complex silicate of boron and aluminium with Fe, Mg, Mn, Ca, Na, K, Li, F and OH) usually occurs as idiomorphic or rounded grains which are pleochroic from yellowish-brown to greenish-brown. In a few cases the pleochroism ranges from greenish-blue to mauve.

Monazite (phosphate of cerium and lanthanum) occurs as pale-yellow squares, with high relief.

Fluorspar (CaF_2) forms cleavage fragments, in some cases tinged with purple.

Sillimanite (Al_2SiO_5) occurs as slender colourless prisms.

Magnetite (Fe_3O_4) occurs as ragged, opaque silvery grains, often stained with limonite.

Limonite ($\text{Fe}_2\text{O}_3\text{Aq}$) occurs as opaque, brown earthy grains, often with cores of magnetite.

Ilmenite ($\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$) occurs as non-magnetic, opaque metallic grains, often coated with leucoxene.

Leucoxene occurs as opaque, white earthy grains.

Microstructure.

The microstructures of all the rocks are characterised by quartzitic aggregates which enclose most of the felspar. In the grits and sandstones the sericite, kaolin and limonite are interstitial to the

¹ Boswell, *loc. cit.*

TABLE III.—*Species Identified in the Heavy-Mineral Assemblages and their Proportions.*

	S1.	S2.	S3.	S3W.	S4.	S5.	S6.	S7.	S8.	S9.	S10.
Zircon . . .	r	a	v.a	a	v.a	v.a	v.a	v.a	v.a	v.a	f
Rutile . . .	r	f	f	f	f	f	f	f	f	f	f
Almandine . .	v.a	r	...	r	...	v.r	v.a
Tourmaline :											
Brown . . .	f	f	f	f	...	f	f	f	f	r	f
Blue	r
Monazite	v.r	...	r	v.r	r	v.r	r	...	v.r	...
Fluorspar	f	f	v.r
Sillimanite	v.r
Magnetite . .	f	f	f	f	f	f	f	f	f	f	a
Limonite . . .	f	f	f	a	f	f	f	f	f	f	f
Ilmenite . . .	f	f	f	f	f	f	f	f	f	f	f
Leucoxene . .	f	a	f	a	f	f	f	f	f	f	f
	S11.	S12.	S13.	S14.	S15.	S16.	S17.	S18.	S19.	S20.	
Zircon . . .	v.a	f	f	r	f	f	v.a	a	v.a	v.a	
Rutile . . .	f	f	f	f	f	f	f	f	f	f	
Almandine . .	v.a	v.a	v.a	v.a	v.a	v.a	...	r	
Tourmaline :											
Brown . . .	f	f	f	f	r	f	f	f	r	r	
Blue	r	
Monazite	
Fluorspar	
Sillimanite	
Magnetite . .	a	f	f	...	f	f	f	
Limonite . . .	f	f	f	f	f	a	a	a	a	f	
Ilmenite . . .	f	f	a	f	a	a	a	
Leucoxene . .	f	f	a	f	a	a	a	a	a	a	
	S21.	S22.	S23.	S24.	S25.	S26.	S27.	S28.	S29.	S30.	
Zircon . . .	f	a	a	f	v.a	f	v.a	f	f	f	
Rutile . . .	f	a	f	f	...	f	f	f	f	f	
Almandine	r	v.a	r	a	r	f	a	...	
Tourmaline :											
Brown . . .	f	f	v.r	r	...	r	v.r	r	f	f	
Blue	
Monazite	v.r	
Fluorspar	
Sillimanite	
Magnetite	f	f	f	...	f	...	f	f	f	
Limonite . . .	a	a	a	a	v.a	a	v.a	
Ilmenite	f	f	f	...	a	...	f	f	f	
Leucoxene . .	a	a	a	a	v.a	a	v.a	f	f	f	

v.a = very abundant; a = abundant; f = frequent; r = rare; v.r = very rare.

aggregates, but in the siltstones the aggregates are isolated in these minerals. In the flaggy rocks muscovite occurs on the bedding planes.

Within these limits the microstructures vary considerably, as will be seen in Figs. 24 to 31. There is, of course, a gradation from one type of microstructure to another.

One of the typical microstructures is characterised by a wide variation in grain size, frequently from 3 or 4 mm. to less than 0.1 mm. In Fig. 24, part of a large grain is shown on one side of the field; the remainder of the field is occupied by smaller quartz grains, more or less intricately sutured together to form quartzitic aggregates, between which is a bond of sericite and/or kaolin. In unweathered examples, this microstructure gives the grit a compact texture, as, for instance, in samples *S4*, *S7* and *S15*. Slightly weathered examples include *S16*, *S28*, *S29*, *S8* and *S5*. Weathering gives the grits a more open texture as, for instance, in *S14* and *S18*. Specimens *S10*, *S11*, *S12* and *S13* are slightly weathered grits with a similar microstructure to that of the examples already cited, though the average grain size is decidedly less.

A more quartzose variation of this microstructure is shown by *S30* (Fig. 25), which contains less sericite and kaolin than most grits.

Another microstructure which occurs frequently is that in which the quartz grains are fairly uniform in size. The quartzitic aggregates are more or less intricately sutured together. *S17* and *S19* (Fig. 26) are fine-grained examples of this type in which the sutures are simple. *S24* is rather coarser and the suturing is more complex. *S21* and *S2* are still coarser; in *S21* the suturing is quite simple (Fig. 27), but in *S2* it is rather more intricate. *S3* is a more quartzitic variety, with simple sutures as shown in Fig. 28. Specimen *S9* is a more quartzose variety with complex sutures (Fig. 29).

The banded structure of a fine-grained, flaggy sandstone is illustrated in Fig. 30, in which a micaceous layer separates two layers of fine-grained sandstone. *S27* is a typical example.

The typical microstructure of the siltstones *S6*, *S20*, *S23* and *S25* is shown in Fig. 31.

IV.—THE MOULDING CHARACTERISTICS OF THE CRUSHED GRITS.

The various characteristics, such as mechanical grading, permeability and green strength, which are used to assess the value of a crushed grit for moulding purposes, depend almost entirely on the petrology of the uncrushed grit. The method by which the grit is crushed is relatively unimportant.

The petrological factors which control the moulding characteristics are :

(a) The mineralogical constitution, that is, the relative proportions of quartz, felspar, mica, kaolin and, in a few cases, limonite also.

(b) The microstructure.

The effects of these factors may be isolated if the grits are divided into groups in which the quartz content is a constant (within the limits of experimental error). In each group the relative proportions of felspar, mica and kaolin can then be plotted on a triangular diagram. As limonite is of importance in a few cases only, its effect can be considered separately. In this way, it is possible to consider the effect of different types of microstructure in grits with similar mineralogical constitutions or *vice versa*.

Mechanical Grading.

The results of the mechanical grading are given in Tables IV. and V. Nearly all the grits were crushed in the laboratory, first in a small jaw-crusher and then by milling until all the grit passed through a British Standards Institution No. 5 sieve. It will be seen from Fig. 8 that there appears to be little difference between the grading of grit prepared by a quarry jaw-crusher and that crushed in the laboratory.

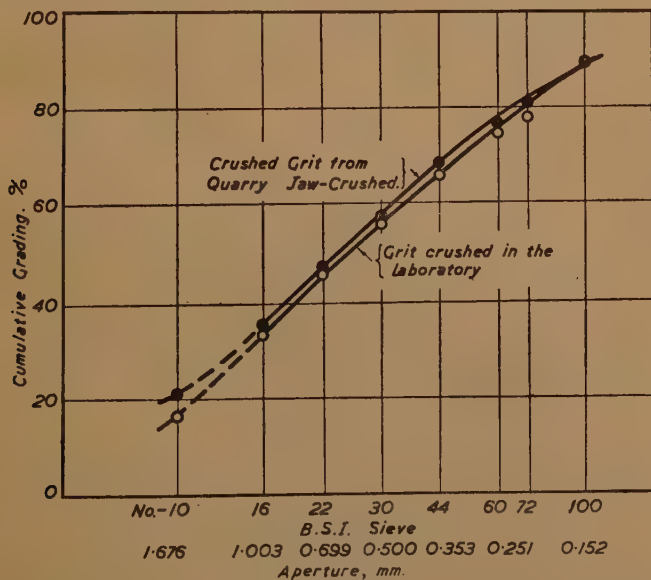


FIG. 8.—The Mechanical Grading of Grit S15 after Crushing.

Typical cumulative grading curves are shown in Figs. 9, 10 and 11. Several forms of grading may be distinguished. They depend mainly on the microstructures of the uncrushed grits, as will be seen from the following summary :

(a) Compact, fairly fresh, fine-grained grits with quartzitic aggregates having simple sutures (see Fig. 26) produce concave

curves, *e.g.*, *S17* and *S19*, Fig. 9. The flat dotted portion corresponds to composite grains, while the steep portion corresponds to the size (0.2–0.3 mm.) of the individual grains in the uncrushed grits.

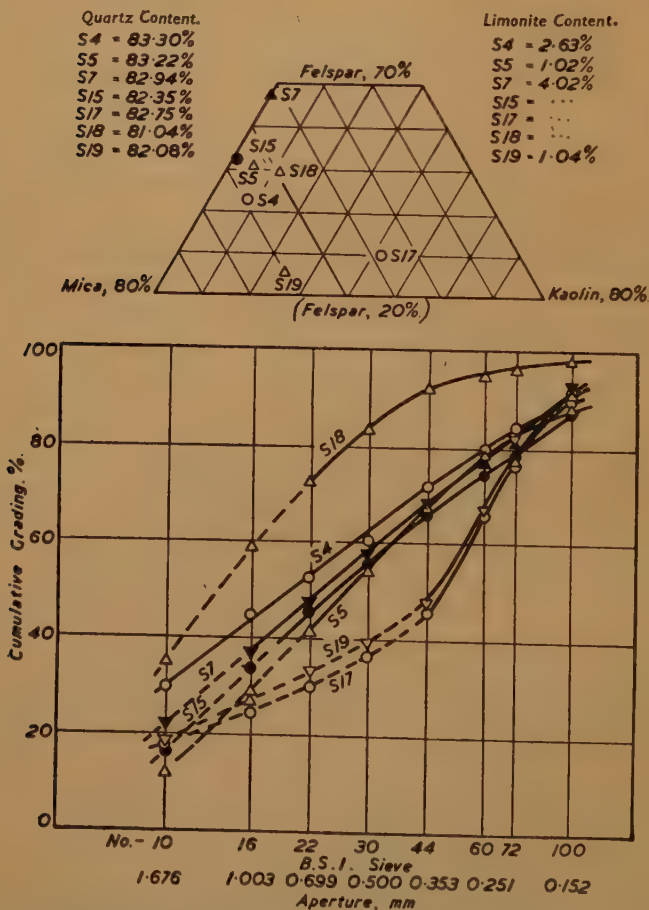


Fig. 9.—The Mechanical Grading of Crushed Grits containing 81–83% of Quartz.

(b) Compact, fairly fresh grits with a widely variable grain size yield almost straight grading curves, *e.g.*, *S4*, *S7* and *S15*, Fig. 9, provided that most of the sericite, kaolin and limonite adhere to the quartz grains (*see* Fig. 24). The variation in position of the three curves corresponds to the difference in

the average grain size. The medium-grained grits *S*10, *S*11 and *S*12, Fig. 10, yield almost straight curves, similar to those for the coarse grits *S*4, *S*7 and *S*15 in positions corresponding to their smaller average grain size.

(c) Podsol-leached, coarse grits with variable grain size yield convex curves, showing that little material passes through the

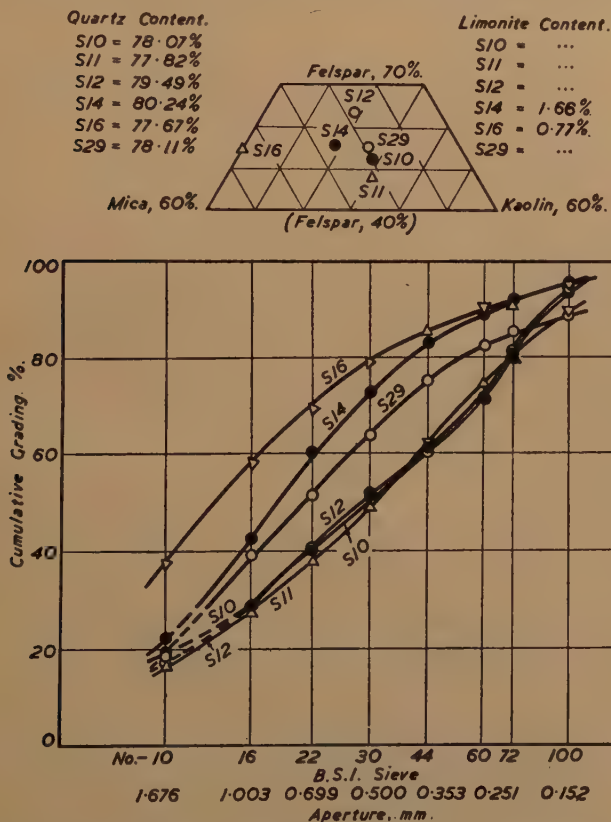


FIG. 10.—The Mechanical Grading of Crushed Grits containing 77–80% of Quartz.

B.S.I. No. 100 sieve, e.g., *S*18, Fig. 9. The process of weathering removes the sericite, kaolin and limonite, leaving the quartzitic aggregates and almost fresh felspar. During crushing the simply-sutured aggregates separate into the individual grains (see Fig. 7) and the felspar breaks along the cleavages. Most of the sutures in the aggregates are simple and the majority of the quartz grains range from 0·3 to 0·7 mm. The intricately-

sutured aggregates yield composite grains corresponding to the dotted portion of the curve. The convexity is accentuated, as *S18* does not show such a wide variation in grain size as some grits, e.g., *S7*, Fig. 9.

(*d*) Coarse, fairly fresh grits with variable grain size and rather open texture (see Fig. 24) yield convex grading curves,

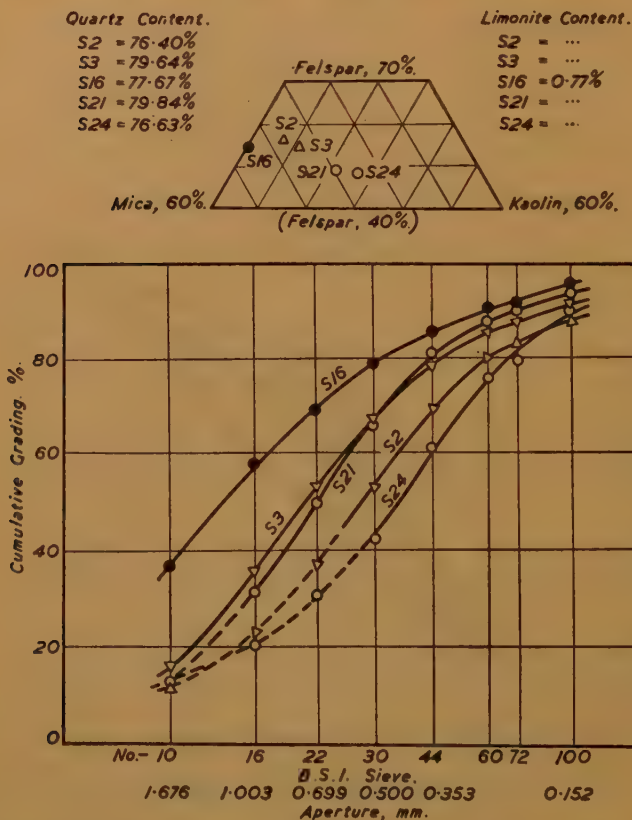


FIG. 11.—The Mechanical Grading of Crushed Grits containing 76–79% of Quartz.

e.g., *S16* and *S29*, Fig. 10. These grits have been weathered just enough to allow the bonding minerals—sericite, kaolin and limonite—to part from the quartz grains. These curves should be compared with those of *S4*, *S7* and *S15*, Fig. 9, in which these minerals adhere to the quartz grains.

(*e*) Coarse, weathered grits in which the weathering has not been of podsol character yield rather steep convex curves,

TABLE IV.—*Sieve Analyses of the Crushed Rocks.*

Rock.	Percentage on B.S.I. Sieve No.—								Per-centage through 100.	Total. %.
	10.	16.	22.	30.	44.	60.	72.	100.		
S2	11.0	11.7	13.5	16.4	15.8	10.1	3.4	5.4	12.8	100.1
S3	16.1	19.7	17.5	14.4	10.7	6.5	1.9	4.2	9.1	100.1
S4	29.1	15.1	8.2	7.9	10.6	8.8	3.6	6.3	10.0	99.6
S5	12.2	15.8	13.2	13.2	13.4	10.2	3.9	7.2	10.1	99.2
S6	19.0	10.5	5.7	4.3	4.8	6.0	2.8	14.8	31.3	99.2
S7	21.3	15.1	10.9	8.8	9.7	10.7	5.3	11.2	6.3	99.3
S8*	18.1	10.1	8.7	8.9	12.5	11.8	1.7	13.5	14.7	100.0
S9	7.4	13.4	13.6	13.7	15.0	12.2	4.9	3.6	15.6	99.4
S10	12.4	7.7	6.6	9.3	17.1	18.1	3.7	8.9	16.2	100.0
S11	15.8	11.4	10.1	11.0	14.1	10.9	7.9	9.3	8.8	99.3
S12	18.2	9.7	12.9	10.4	10.0	8.6	11.7	13.6	5.1	100.2
S13*	25.4	7.2	4.7	5.0	8.5	13.6	9.5	13.7	12.3	99.9
S14	21.5	20.5	17.2	13.2	10.2	6.1	3.9	3.1	3.9	99.6
S15	16.6	17.1	12.0	9.5	10.7	8.3	3.6	11.6	10.4	99.8
S15*	21.0	14.1	11.6	10.6	10.8	8.1	4.1	8.7	11.2	100.2
S16	36.9	20.5	11.8	8.4	7.5	4.2	2.1	3.7	4.9	100.0
S17	17.3	6.2	5.9	5.8	9.5	21.0	10.9	15.7	7.5	99.8
S18	34.8	23.7	14.4	10.6	8.7	3.1	0.8	2.0	1.8	99.9
S19	18.2	9.4	6.0	5.5	8.1	18.6	11.6	14.2	8.5	100.1
S20	18.2	11.1	5.9	4.0	4.2	4.1	3.3	25.3	23.3	99.4
S21	13.1	18.3	18.8	15.7	15.4	6.5	1.8	5.2	5.1	99.9
S22	17.3	11.0	8.9	10.1	19.7	13.9	4.1	7.4	7.4	99.8
S23	42.2	13.5	5.2	3.0	2.2	1.1	3.5	7.9	20.9	99.5
S24	11.7	9.2	9.1	11.7	18.5	14.2	3.8	10.4	11.3	99.9
S25	12.3	30.0	14.4	6.1	3.9	3.5	2.8	8.0	18.7	99.7
S26	16.9	14.9	12.5	11.5	13.5	9.3	3.5	9.9	8.0	100.0
S27	30.3	13.2	5.6	3.6	4.3	3.8	2.1	19.4	16.0	99.3
S28*	18.4	13.9	9.7	12.2	15.6	12.1	3.6	10.1	4.8	100.3
S29	16.0	22.4	12.9	11.5	11.1	7.8	2.7	5.3	10.6	100.3
S30	10.3	9.3	11.6	9.7	15.3	17.8	7.4	10.7	8.0	100.1

* Grit crushed at quarry.

with little material passing through the B.S.I. No. 100 sieve, *e.g.*, S14, Fig. 10. Such grits usually have a deep-red hue and are rather friable. They have weathered under conditions such that the sericite has been partly replaced by hydrated iron oxide and kaolin. These replacement minerals adhere closely to the quartz grains and consequently there is only a small proportion of "fines." This convexity is accentuated, as S14 does not show such a wide variation in grain size as some grits, *e.g.*, S7, Fig. 9.

(f) Fresh, medium-to-coarse grits with uniform grain size and having a rather open texture (*see* Figs. 26 to 28) yield S-shaped curves, *e.g.*, S2, S3, S21 and S24, Fig. 11. The steeper parts of these curves correspond to the average grain size. The relative positions of S2 and S24 are in accord with the increase in grain size already noted in the micro-

TABLE V.—*Cumulative Grading of the Crushed Rocks.*

Rock.	Percentage on B.S.I. Sieve No.—							
	10.	16.	22.	30.	44.	60.	72.	100.
S2	11.0	22.7	36.2	52.6	68.4	78.5	81.9	87.3
S3	16.1	35.8	53.3	67.7	78.4	84.9	86.8	91.0
S4	29.1	44.2	52.4	60.3	70.9	79.7	83.3	89.6
S5	12.2	28.0	41.2	54.4	67.8	78.0	81.9	89.1
S6	19.0	29.5	35.2	39.5	44.3	50.3	53.1	67.9
S7	21.3	36.4	47.3	56.1	65.8	76.5	81.8	93.0
S8*	18.1	28.2	36.9	45.8	58.3	70.1	71.8	85.3
S9	7.4	20.8	34.4	48.1	63.1	75.3	80.2	83.8
S10	12.4	20.1	26.7	36.0	53.1	71.2	74.9	83.8
S11	15.8	27.3	37.3	48.3	62.4	73.3	81.2	90.5
S12	18.2	27.9	40.8	51.2	61.2	69.8	81.5	95.1
S13*	25.4	32.6	37.3	42.3	50.8	64.4	73.9	87.6
S14	21.5	42.0	59.2	72.4	82.6	88.7	92.6	95.7
S15	16.6	33.7	45.7	55.2	65.9	74.2	77.8	89.4
S15*	21.0	35.1	46.7	57.3	68.1	76.2	80.3	89.0
S16	36.9	57.4	69.2	77.6	85.1	89.2	91.4	95.1
S17	17.3	23.5	29.4	35.2	44.7	65.7	76.6	92.3
S18	34.8	58.5	72.9	83.5	92.2	95.3	96.1	98.1
S19	18.2	27.6	33.6	39.1	47.2	65.8	77.4	91.6
S20	18.2	29.3	35.2	39.2	43.4	47.5	50.8	76.1
S21	13.1	31.4	50.2	65.9	81.3	87.8	89.6	94.8
S22	17.3	28.3	37.2	47.3	67.0	80.9	85.0	92.4
S23	42.2	55.7	60.9	63.9	66.1	67.2	70.7	78.6
S24	11.7	20.9	30.0	41.7	60.2	74.4	78.2	88.6
S25	12.3	42.3	56.7	62.8	66.7	70.2	73.0	81.0
S26	16.9	31.8	44.3	55.8	69.3	78.6	82.1	92.0
S27	30.3	43.5	49.1	52.7	57.0	60.8	62.9	83.3
S28*	18.4	32.3	42.0	54.2	69.8	81.9	85.5	95.5
S29	16.0	38.4	51.4	62.8	73.9	81.7	84.4	89.7
S30	10.3	19.6	31.2	40.9	56.2	74.0	81.4	92.1

* Grit crushed at quarry.

structures (see "Microstructure" above). The positions of S3 and S21 relative to those of S2 and S24 correspond to the higher quartz content of the former.

Expressed in general terms, the cumulative-grading curves of the crushed grits tend to be S-shaped. This form is most marked in grits which, before crushing, were characterised by uniform grain size, slightly weathered bonding minerals, rather open texture and quartzitic aggregates with simple suturing only. When the grain size of the uncrushed grit varies considerably, the quartzitic aggregates are intricately sutured and the rock is fresh, then the central part of the curve becomes flatter.

A sample of crushed grit (Northern Sand) from Tow Law, Durham,¹ which is in use at a steel foundry, contains about twice as much silt and clay as the grits discussed above.

¹ "First Report of the Moulding Materials Sub-Committee," *loc. cit.*, p. 197.

The cumulative grading curves for the siltstones *S6*, *S20*, *S23* and *S25* and the flaggy sandstone *S27* would, if plotted, only show the proportion of composite grains, which is dependent on the amount of milling.

Weathered samples were collected from the tips of certain quarries, *viz.*, *S9* and *S26*. These samples contain a proportion of subsoil, and consequently cannot be related to the microstructure. *S8* and *S28* are samples of crushed quarry waste and contain a proportion of subsoil or clay.

The microstructure of *S22* is too variable for any conclusions to be drawn concerning mechanical grading.

S30 (see Fig. 25) is far more quartzitic than the rest of the grits and its mechanical grading depends more on the conditions of milling than on the microstructure. The result is an almost straight grading curve the position of which is proportional to the amount of milling.

TABLE VI.—*Mechanical Properties of the Crushed Rocks.*


Rock.	Natural Crushed Grit.				Grit with 7.5% of Ball Clay added.			
	Green Strength. Lb. per sq. in.	Water Content. %.	Per-meability Number.	Bulk Density. G. per c.c.	Green Strength. Lb. per sq. in.	Water Content. %.	Per-meability Number.	Dry Strength. Lb. per sq. in.
<i>S2</i>	1.9	5	159	1.55	4.8	5	105	26
<i>S3</i>	1.6	7	276	1.60	4.9	5	264	135
<i>S4</i>	3.8	6	54	1.70	8.9	5	58	180
<i>S5</i>	2.6	5	96	1.70	9.3	6	115	110
<i>S6</i>	5.1	6	14	1.60	8.6	5	22	50
<i>S7</i>	2.6	6	87	1.65	5.7	6	112	62
<i>S8</i>	3.8	4	52	1.55	8.9	5	62	68
<i>S9</i>	6.0	6	63	1.65	8.0	6	99	65
<i>S10</i>	2.6	6	119	1.60	4.8	5	129	44
<i>S11</i>	2.1	5	143	1.70	3.7	5	120	53
<i>S12</i>	1.9	5	91	1.65	5.7	4	68	78
<i>S13</i>	3.5	5	126	1.65	6.4	6	98	82
<i>S14</i>	2.7	6	119	1.70	5.6	6	146	60
<i>S15</i>	2.7	6	132	1.65	5.7	5	144	43
<i>S16</i>	2.1	5	139	1.55	5.4	4	128	78
<i>S17</i>	4.0	6	42	1.65	7.5	6	46	103
<i>S18</i>	2.1	5	185	1.65	5.1	5	167	47
<i>S19</i>	3.8	5	54	1.60	8.0	6	58	64
<i>S20</i>	5.3	7	25	1.70	7.3	8	23	120
<i>S21</i>	2.2	5	98	1.65	5.9	5	64	55
<i>S22</i>	1.9	6	73	1.65	6.8	5	80	104
<i>S23</i>	7.2	5	29	1.75	9.8	7	49	154
<i>S24</i>	2.9	5	54	1.65	6.2	4	56	59
<i>S25</i>	6.2	5	23	1.70	11.9	5	31	25
<i>S26</i>	0.96	5	98	1.65	5.9	6	80	30
<i>S27</i>	6.1	5	30	1.70	9.7	5	34	28
<i>S28</i>	5.3	6	44	1.70	8.9	5	46	32
<i>S29</i>	1.8	5	332	1.70	7.6	5	280	40
<i>S30</i>	1.8	4	150	1.70	4.6	5	120	35

Green Strength and Permeability.

These two characteristics are considered together, as they are closely related. The green strength is greatest when the grains are small and angular, that is, when the grains interlock most. The permeability is greatest when the grains are large and well-rounded, that is, when the grains interlock least. This relationship has long been recognised in the study of moulding sands.¹

The values of the maximum green strength are given in Table VI., together with the corresponding water content, permeability number² and bulk density. If the maximum green strength is plotted against the corresponding permeability number, as in Fig. 12, the relationship between the two is seen to be very close.

Under the head "Microstructure" above, the grits were divided into groups according to their microstructure. The series in which each grit is characterised by uniform grain size, is :

Siltstones	S23, S25, S27, S20.	 Increasing grain size.
Fine-grained sandstones	S19, S17.	
Medium-to-coarse grits	S24.	
	S21, S2.	
	S3.	

A curve can be drawn through these points in the order given (see Fig. 12, curve (a)). As will be seen from the composition diagram, Fig. 11, S21 contains more kaolin than S2, and this difference probably accounts for the higher green strength and lower permeability of the former.

It may thus be possible to predict the green strength and permeability number of a crushed grit from an examination of the microsection of the uncrushed rock, provided that the grain size is fairly uniform.

In the case of grits with variable grain size, the relationship is not so close, but is suggested by curve (b) in Fig. 12. Such grits tend to form more angular grains than those with uniform grain size. Consequently, for a given permeability, they have a slightly higher green strength. It will be seen that points marked as solid circles corresponding to these grits lie to the right of the curve (a), as is to be expected. The difference between the permeability of S7 and that of S15 may be accounted for by the wider variation in grain size of the latter.

The three grits S10, S11 and S12 remain to be considered. These grits show some variation in grain size. As will be seen from the composition diagram, Fig. 10, S12 contains decidedly

¹ Boswell, *loc. cit.*, p. 50.

² The green strength was determined on A.F.A. test-pieces rammed three times. The permeability number was determined on the British Cast Iron Research Association air permeability apparatus, and is expressed as the number of cubic centimetres of air which flow through a sample 1 sq. cm. in cross-sectional area and 1 cm. long when the pressure gradient between the ends of the test-piece is 1 cm. of water per cm.

less kaolin than S10 and S11, thus accounting for its rather lower green strength.

As shown in Table VI., the addition of 7.5% of ball clay to the crushed grit improves the green strength considerably without, in many cases, seriously altering the permeability. Thus there is considerable scope for the use of crushed grits as semi-synthetic moulding sands by the addition of a small proportion of bond. Alternatively, the crushed grit could be blended with a sand containing too much bond to be used alone for steel moulding.

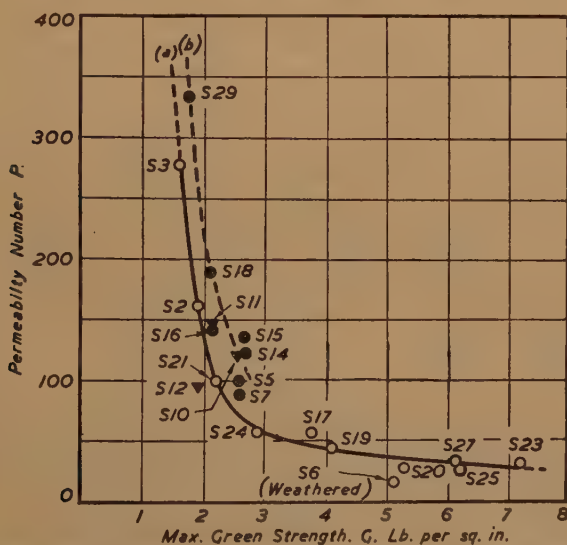


FIG. 12.—The Relation between Permeability and Green Strength.

The dry strengths of the crushed grits bonded with 7.5% of ball clay are comparable with those of steel moulding sands.

Refractoriness.

The results of the firing tests are recorded in Table VII. They are best considered in the same groups as those used for Figs. 9 to 11. The cylinders (American Foundrymen's Association standard form) were fired at 1550° C. for 2 hr. Texture is described as very open, open, compact, or very compact, corresponding to the progressive reduction in permeability due to fritting. The glaze is referred to as intergranular (exterior of specimen unglazed), slight, or marked (exterior of specimen more or less glazed). The cracking is described as incipient, slight, or marked. When tapped, some of the cylinders gave a dull note, while others gave a brittle note, rather like that of a silica-brick.

TABLE VII.—*Refractoriness.*

Rock.*	Shrinkage.	Texture.	Colour.	Glaze.	Cracking.	Note.
<i>Grits with 81-83% of Quartz. Fig. 9.</i>						
S4 U.	Shrank badly.	Compact.	Brown.	Slight.	Incipient.	Dull.
B.	"	Very compact.	"	Marked.	Slight.	"
S5 U.	2.5%	Open.	Brown, mottled.	Slight.	Incipient	"
B.	7.5%	Compact.	"	Marked.	"	"
S7 U.	Shrank badly.	Open.	"	Intergranular.	"	Brittle.
B.	"	"	"	"	"	"
S15 U.	"	"	Faint brown.	Slight.	"	"
B.	2.5%	"	"	"	"	"
S18 U.	"	Open.	Brown, mottled.	Slight.	Friable.	Brittle.
B.	5%	"	"	"	"	"
S17 U.	5%	Open.	Faint brown.	Intergranular.	Incipient.	Dull.
B.	15%	"	"	"	"	"
S19 U.	Distorted.	"	"	Slight.	Slight.	"
B.	"	"	"	Marked.	Marked.	"
<i>Grits with 77-80% of Quartz. Fig. 10.</i>						
S10 U.	7.5% 1580°C.	Open.	White.	Intergranular.	Marked.	Dull.
B.	17.5%	"	"	"	"	"
S11 U.	"	"	"	"	Incipient.	Brittle.
B.	"	"	"	"	"	"
S12 U.	2.5%	"	"	"	Friable.	"
B.	7.5%	"	"	"	"	"
S14 U.	7.5%	Open.	Brown, mottled.	Intergranular.	Incipient.	Brittle.
B.	Distorted.	"	"	Slight.	"	"
S16 U.	7.5%	"	White.	Intergranular.	Friable.	"
B.	12.5%	"	"	Slight.	"	"
S29 U.	2.5%	Very open.	Brown, mottled.	Intergranular.	"	"
B.	2.5%	"	"	"	"	"
<i>Grits with 76-79% of Quartz. Fig. 11.</i>						
S2 U.	0.0%	Open.	White.	Intergranular.	Marked.	Dull.
B.	7.5%	"	"	Slight.	"	"
S3 U.	2.5%	"	"	Intergranular.	None.	Brittle.
B.	5.0%	"	"	Slight.	"	"
S21 U.	0.0%	"	"	Intergranular.	Friable.	"
B.	2.5%	"	"	"	"	"
S24 U.	5.0%	}	Brown, mottled.	Slight.	Incipient	"
B.	7.5%					

* U. = unbonded; B. = bonded.

In each case, the addition of bond makes the specimen more vesicular, *i.e.*, it is less permeable and more glazed and contracts more. In addition it accentuates any tendency towards cracking.

It will be seen from the Table that a mechanical grading like that of *S3* and *S21* (Fig. 11) gave the most satisfactory results. Although there is some variation in detail, it is generally true that the central portion of the curve should be steep, that is, the bulk of the crushed grit should consist of two sizes of particle only. Quartz grains, together with some felspar, constitute most of the coarse fraction, while the fine fraction is composed mainly of sericite, kaolin and limonite, together with finely-divided quartz and felspar.

This type of grading is best developed in *S2*, *S3*, *S21* and *S24*. It will be noticed that *S2* and *S24* are not so satisfactory when fired as *S3* and *S21*, an observation which is in accord with the lower quartz content of the former.

The convex curves of *S18* and *S19* correspond to the upper part of an S-shaped curve and, as might be expected, their resistance to firing is fairly satisfactory.

The siltstones, being composed of small quartz grains and containing a particularly high proportion of sericite, kaolin and limonite, have a low refractoriness. *S6*, for instance, melted and flowed over the furnace floor.

The microstructures of a typical siltstone (*S6*) and a typical grit (*S1*) after firing are shown in Figs. 32 and 33 respectively. The grey spots in the former are the ghosts of quartz grains now completely vitrified. The corresponding spots in Fig. 33 are larger and still contain a considerable proportion of crystalline silica.

Fig. 34 shows how the quartz grains fracture along the slip-planes and so facilitate fritting. In other words, quartz grains with linearly-arranged bubble inclusions are not so satisfactory as those in which the inclusions are scattered irregularly.

Weathering decreases the refractoriness of a crushed grit unless it is severe enough to leach away the decomposition products. It tends to increase the proportion of low-temperature, hydrated minerals—sericite, kaolin and limonite. During firing, these minerals act as fluxes and so promote the fritting of the quartz grains. The presence of fresh feldspar is less detrimental.

V.—CONCLUSION.

The influence of the petrology of a grit on its moulding characteristics has been discussed and the various conclusions have been summarised. It now remains to state the petrology of the type of grit most likely to be useful for steel moulding purposes. The important features of such a grit are :

(a) The grains should be of uniform size; this size should be between 0.3 and 1.0 mm. The maximum green strength and the corresponding permeability number may be determined from the graph, Fig. 12, curve (a).

(b) The suturing of the quartzitic aggregates should be simple, so that the proportion of composite grains will be small.

(c) The quartz grains should be as free as possible from strain, whether indicated by slip-planes or by strain shadows.

(d) A quartz content of 80% seems desirable.

(e) The proportion of sericite, kaolin and limonite should be fairly low if high refractoriness is to be maintained. This permits the addition of clay bond to secure any desired range of moulding properties.

(f) The feldspar content should not be large, though 10% does not seriously affect the general characteristics.

The grits which conform to this definition are *S3* and *S21*. The coarse, podsol-leached grits *S18* and *S29* are fairly satisfactory.

S2 and S24 are not so satisfactory, but might be improved by blending. S17 and S19 might be useful as blending agents for mixtures requiring more bond.

The authors wish to thank Dr. K. W. Gee for assistance in the sieving analyses of the crushed rocks.

APPENDIX A.—*Detailed Petrographical Descriptions of the Rock Samples, S1–S30.*

S1, Crawshaw Sandstone. *Middlewood Quarry, near Sheffield.*

Locality.—Quarry adjoining by-road from Oughtibridge to Worrall, 1 mile south of Oughtibridge.

Owner.—Messrs. Jas. Turner, Ltd., Middlewood Quarries, near Oughtibridge.

Petrological Description.

The rock at this quarry is a pale-brown, medium-grained felspathic grit or arkose, containing a few quartzite pebbles.

It is composed of quartz, felspar and sericite. The quartz occurs as subangular grains, mostly less than 0.5 mm. in dia., though a few grains are as much as 1.0 mm. in dia. In most of the quartz grains, the bubble inclusions are scattered irregularly and strain shadows are rare. Many of the grains show signs of secondary silicification. The felspar occurs as rounded grains; it is chiefly microcline micropertthite, together with some medium plagioclase, and is rather decomposed. The sericite occurs as fibrous aggregates, often on a coarse scale; it is slightly iron-stained.

The microstructure is characterised by large quartzitic aggregates, which enclose most of the felspar grains. Some of the sericite occurs as thin films separating the grains in the quartzitic aggregates, but most of it is interstitial.

A micrometric analysis of the sandstone gave the following results :

Quartz	86.60%
Microcline micropertthite and plagioclase	9.00%
Sericite	4.43%
	<hr/> 100.03%

A sample of the rock was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was almost white and was composed of subangular, clean grains, only a few having a coating of limonite. Felspar grains were not numerous.

Heavy Minerals.—0.08% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Garnet : Very abundant; rounded grains of pink almandine.

Tourmaline : Frequent; brown pleochroic ragged grains.

Rutile : Rare; dark-red irregular grains.

Zircon : Rare; rounded grains.

Magnetite : Frequent; opaque grey grains.

Ilmenite : Frequent; opaque, rather leucoxenised grains.

Limonite : Frequent; brown earthy grains.

S2, Kinderscout Grit. *Leam Quarry, near Hathersage.*

Locality.—Adjoining the Hathersage-Grindleford road at Leam Wood, 1½ miles south-south-east of Hathersage Station.

Owner.—Quarry disused.

Petrological Description.

The grit at this locality is a pale-brown, medium-grained arkose. It occurs as well-jointed beds, several feet thick, though in some parts of the quarry it is rather flaggy. The grit is remarkably uniform in grain size over the whole of the face.

Microscopic examination shows that the grit consists of angular to subangular grains of quartz and felspar, together with interstitial kaolin and sericite. Though there are some composite quartz grains, most of the quartz occurs as large, single grains, up to 1.5 mm. across, more or less strained and traversed by lines of bubbles. The felspar is mainly unaltered microcline with micropertthitic structure, though there is some sericitised acid plagioclase. Most of the sericite is iron-stained, suggesting that it is decomposing. There are one or two flakes of muscovite.

The microstructure of the grit is dominated by quartzitic aggregates, some of which have sericitic films along the sutured junctions of the constituent grains. Some of the felspar grains are enclosed in the quartzitic aggregates, but most of the felspars lie between them. The kaolin and most of the sericite are interstitial to the quartz and felspar.

A micrometric analysis of the grit gave the following composition :

Quartz	76.40%
Microcline micropertthite and plagioclase	13.08%
Mica (sericite and muscovite)	8.51%
Kaolin	2.00%
	<hr/>
	99.99%

A bulk sample of the grit was crushed in the laboratory. It was found that the grit remaining on the 0.5 mm. sieve contained very little felspar. After rinsing, the grit that passed through the 0.5-mm. sieve and remained on the 0.25-mm. sieve was slightly brown in mass and contained very few felspar grains; most of the quartz grains were subangular and had a thin coating of hydrated iron oxide.

Heavy Minerals.—0.08% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon: Abundant; prismatic with rounded pyramidal terminations, sometimes faintly tinged with mauve.

Rutile: Frequent; dark-red irregular grains or prisms with rounded ends.

Tourmaline: Frequent; brown pleochroic stumpy prisms with jagged ends; several blue-green grains.

Fluorspar: Frequent; pale-violet cleavage fragments.

Monazite: Very rare; yellow squares with dark edges.

Magnetite: Frequent; opaque silver-grey grains.

Ilmenite: Frequent; opaque, rather leucoxenised grains.

Leucoxene: Abundant; opaque, earthy white or yellowish-brown rounded grains.

S3, Upper Burbage Grit. *Surprise Quarries, near Hathersage.*

Locality.—Overlooking the main Sheffield-Hathersage road at the Surprise View, $1\frac{1}{2}$ miles south-east of Hathersage.

Owner.—Mr. A. Siddall, Millstone Edge Quarries, Hathersage, via Sheffield.

Petrological Description.

The grit exposed in these quarries is a typical arkose, faintly tinged with pink. It occurs as beds from 3 to 10 ft. in thickness, showing marked current-bedding. These beds consist mainly of medium-grained grit, which, in the hand specimen, appears as an aggregate of clear, glassy quartz grains and pink, opaque feldspars. Near the base of each bed there is a transition from the medium-grained grit into a layer of conglomerate, a few inches thick, composed of pebbles of quartzite and feldspar, $\frac{1}{2}$ in. or more across. There appears to be rather more feldspar in the conglomerate than in the medium-grained grit. The tops of most of the beds are fine-grained.

Microscopic examination shows that the medium-grained grit in the quarry face consists of angular grains of quartz and microcline feldspar, together with interstitial sericite and kaolin; there are one or two flakes of muscovite and a few small patches of carbonate. Most of the quartz grains are large single ones, up to 1.5 mm. across, more or less strained, and traversed by bubbles; quartzite grains are rare. With the exception of a little feldspar associated with the interstitial sericite, the feldspar is but slightly decomposed and no pseudomorphs after feldspar were found. The feldspar is microcline microperthite the composition of which is about 80% potash-feldspar and 20% soda-feldspar. The sericite is iron-stained.

The microstructure of the grit is characterised by quartzitic aggregates. Some of the feldspar and quartz grains are sheathed with sericite. Kaolin and most of the sericite occur as interstitial patches.

A micrometric analysis of the grit gave the following composition :

Quartz	79.64%
Microcline microperthite	11.02%
Mica (sericite and muscovite)	6.96%
Kaolin	2.39%
	<hr/>
	100.01%

A sample of the weathered rock on the quarry tip was examined. This weathered grit is very crumbly and is stained a reddish-brown. Microscopic examination of this grit showed that there were extensive patches of opaque hydrated iron oxides, whereas the quantity of opaque minerals in the fresh grit is negligible. Apparently the effect of weathering is to cause the sericite to decompose, for the more advanced the weathering, the more iron-stained is the sericite. The kaolin is difficult to detect in the weathered grit; so far as can be seen in the microsections, the hydrated iron oxides, liberated by the weathering, appear to have intermingled with the kaolin and made it opaque. The weathering has not made much difference to the large feldspar grains. If the opaque patches are assumed to

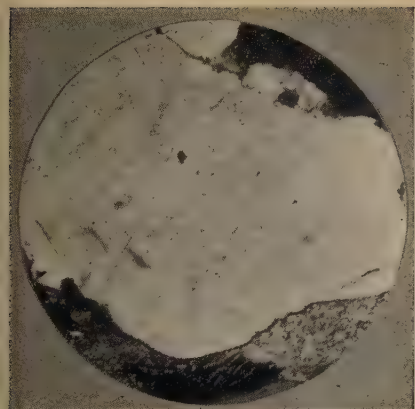


FIG. 13.—Quartz Grain containing sub-parallel lines of bubbles.

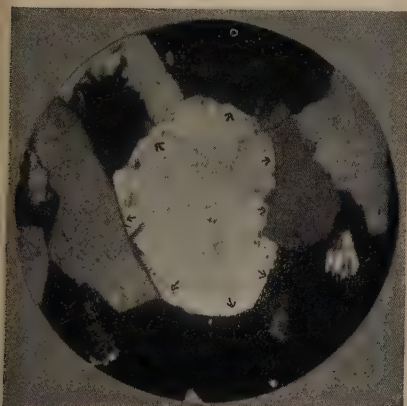


FIG. 14.—Quartz Grain coated with secondary silica. Original outline indicated by arrows.

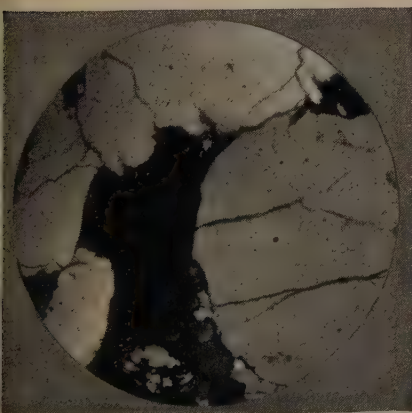


FIG. 15.—Quartz Grain fractured by frost action.
FIGS. 13 to 15.—The Quartz of the Millstone Grits.
× 100, crossed nicols.

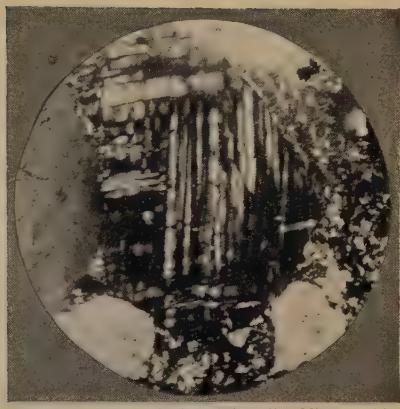


FIG. 16.—Rounded Grain of Microcline Microperthite Felspar. × 100, crossed nicols.

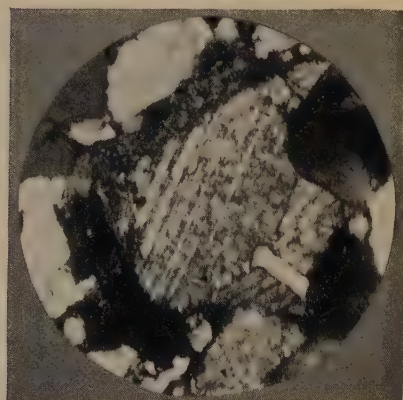


FIG. 17.—Grain of Partly Decomposed Plagioclase Felspar. × 100, crossed nicols.

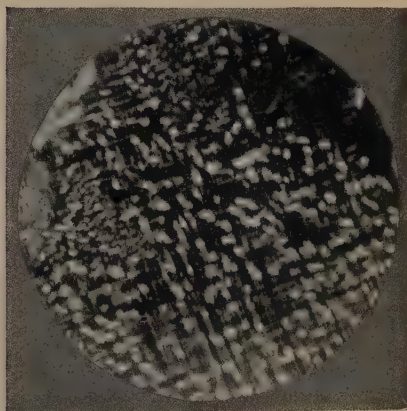


FIG. 18.—Microperthitic Structure in a Felspar.
× 250, crossed nicols.

FIGS. 16 to 18.—The Felspars of the Millstone Grits
(see also Figs. 19 and 20).

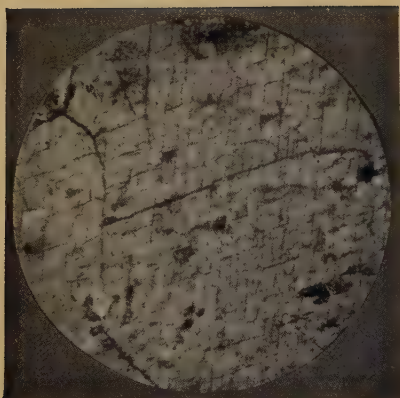


FIG. 19.—Traces of Cleavage Planes in Feldspar. $\times 250$, crossed nicols.

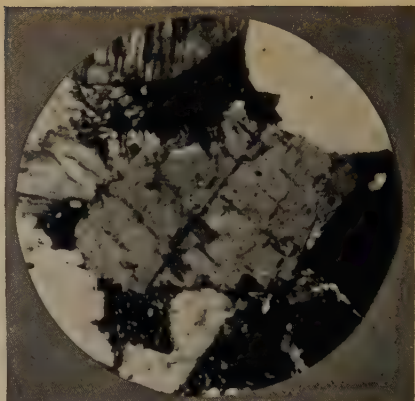


FIG. 20.—Sericitisation along Cleavage Planes in a Feldspar Grain. $\times 100$, crossed nicols.

FIGS. 19 and 20.—The Feldspars of the Millstone Grits (*see also* Figs. 16 to 18).

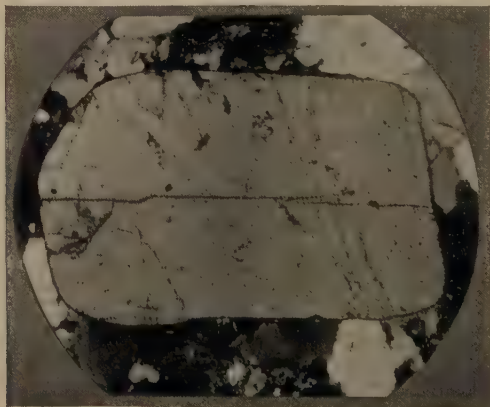


FIG. 21.—A Typical Fresh Micropertthitic Feldspar from a grit which had been thoroughly weathered under podsol conditions (S18). $\times 30$, crossed nicols.

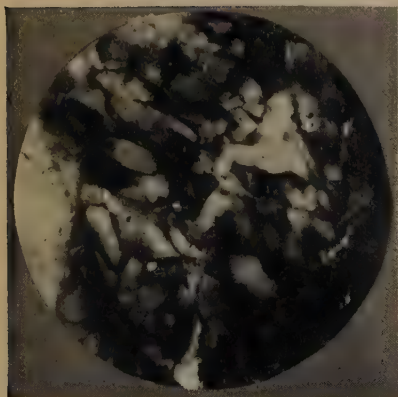


FIG. 22.

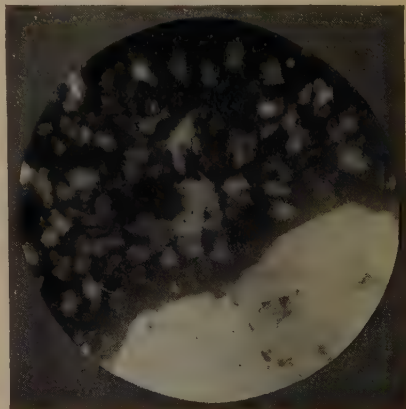


FIG. 23.

FIGS. 22 and 23.—Pockets of Vermicular Kaolin. $\times 250$, crossed nicols.

(Micrographs reduced to four-fifths linear in reproduction.) [Davies & Rees (Part 1).]

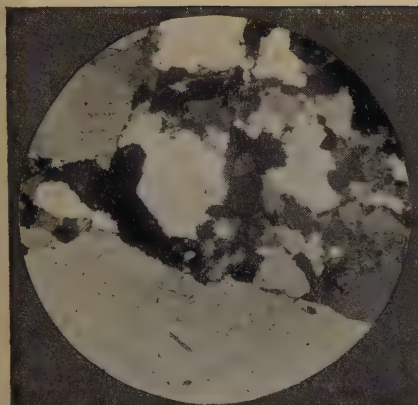


FIG. 24.—Wide Variation in Grain Size in a Typical Grit (S16).

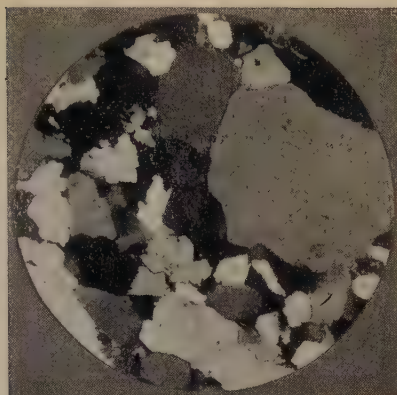


FIG. 25.—Wide Variation in Grain Size in a Quartzose Grit (S30).

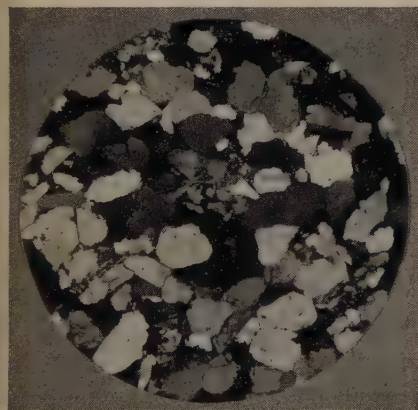


FIG. 26.—Uniform Grain Size in Fine-Grained Grit (S19).

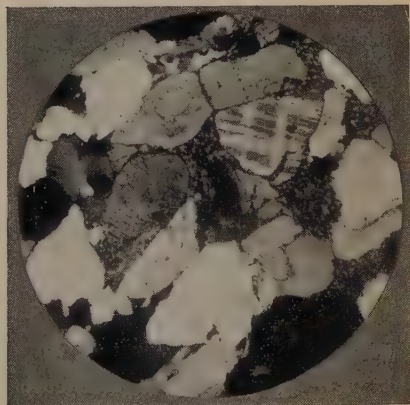


FIG. 27.—Typical Grit of Uniform Grain Size with simply-sutured quartzitic aggregates (S21).

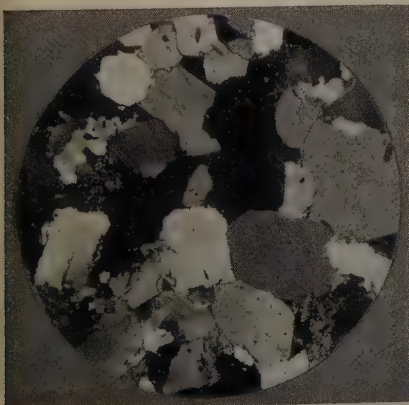


FIG. 28.—Quartzose Grit with simply-sutured quartzitic aggregates (S3).

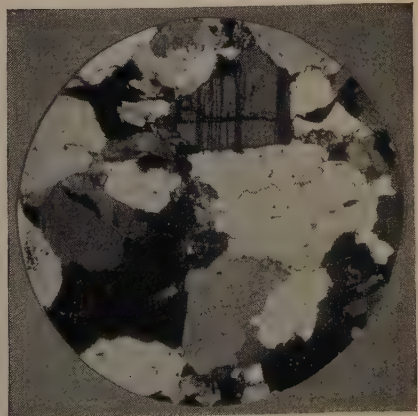


FIG. 29.—Quartzose Grit with intricate suturing of quartzitic aggregates (S9).

FIGS. 24 to 29.—Types of Microstructures (*see also* Figs. 30 and 31). $\times 30$, crossed nicols.

(Micrographs reduced to four-fifths linear in reproduction.) [Davies & Rees (Part 1).]

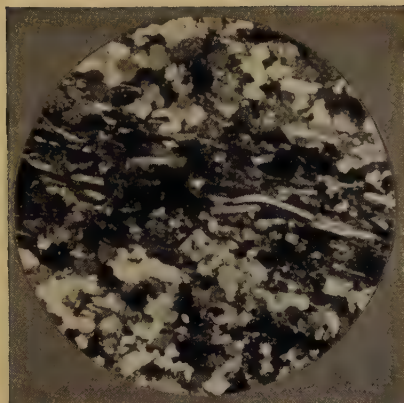


FIG. 30.—Micaceous Band in a Flaggy Sandstone (S27).

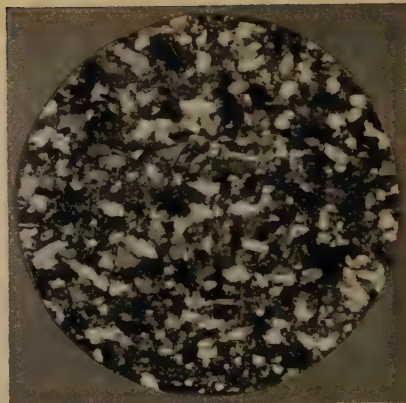


FIG. 31.—Microstructure of a Typical Siltstone (S23).

FIGS. 30 and 31.—Types of Microstructures (see also Figs. 24 to 29). $\times 30$, crossed nicols.

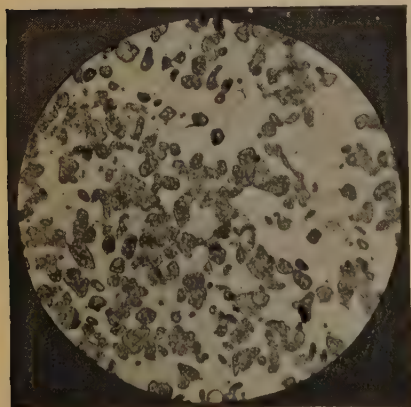


FIG. 32.—Microstructure of a Crushed Siltstone after 2 hr. at 1550° C. (S6).

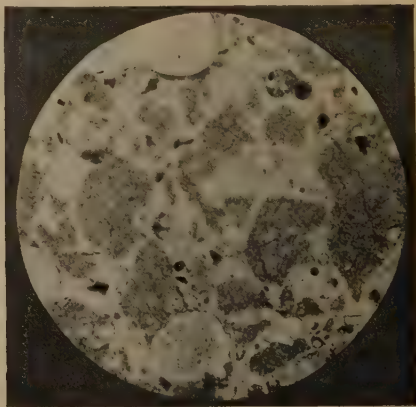


FIG. 33.—Microstructure of a Crushed Grit after 2 hr. at 1550° C. (S1).

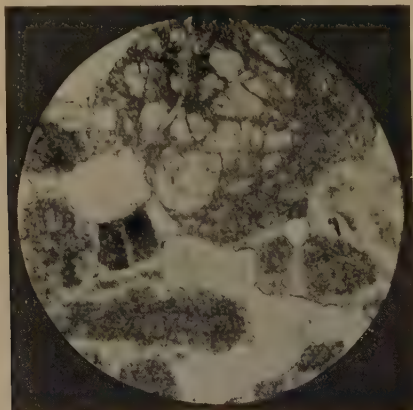


FIG. 34.—Fracturing in a Quartz Grain caused by heating at 1550° C. (S1).

FIGS. 32 to 34.—Microstructures of Crushed Grits after Firing. $\times 30$, ordinary light.

(Micrographs reduced to four-fifths linear in reproduction.) [Davies & Rees (Part 1).

[To face p. 41 R.

have a density of 3.5, then the micrometric analysis of the weathered rock is :

Quartz	63.98%
Microcline microperthite	9.52%
Mica (sericite and muscovite)	8.93%
Kaolin and opaque minerals	17.56%
	<hr/>
	99.99%

Examination of the grits, both unweathered and weathered, shows that crushing makes the felspar more finely-divided than the quartz, owing to the good cleavages in the former mineral. The crushed grit¹ which passed through a 0.5-mm. sieve and remained on the 0.25-mm. sieve was rinsed with water. The unweathered grit so treated was faintly pink in mass and consisted of clear glassy, angular-to-subangular quartz grains, together with some pink felspar grains. The weathered grit so treated was a pale reddish-brown and consisted of glassy, angular-to-subangular quartz grains partially coated with hydrated iron oxides; felspar grains were rare.

Heavy Minerals.—0.05% of heavy minerals was found in a sample of the crushed unweathered grit. The mineral species identified were :

Zircon: Very abundant; prismatic with rounded pyramidal terminations.

Rutile: Frequent; dark-red irregular grains, rarely prismatic.

Tourmaline: Frequent; greenish-brown, bottle-green or violet stumpy prisms.

Sillimanite: Very rare; slender prisms.

Magnetite: Frequent; opaque silver-grey grains.

Ilmenite: Frequent; opaque, rather leucoxenised grains.

The crushed weathered grit contained 1.00% of heavy minerals. This figure is too high, as the heavy residue contained many quartz grains coated with limonite. The species identified in the weathered grit were :

Zircon: Abundant; prismatic with rounded pyramidal terminations.

Rutile: Frequent; dark-red irregular grains.

Tourmaline: Frequent; greenish-brown or bottle-green stumpy prisms.

Monazite: Rare; yellow rectangular grains.

Magnetite: Frequent; stained with limonite.

Ilmenite: Frequent; all grains coated with leucoxene.

S4, Rivelin Grit. Bell Hagg Quarry, near Sheffield.

Locality.—Adjoining the main Sheffield-Ashopton-Manchester road, $\frac{3}{4}$ mile west of Crosspool.

Owner.—Messrs. J. Andrews & Son, Bell Hagg Quarry, Crosspool, Sheffield.

Petrological Description.

The grit in this quarry is extremely variable in character, though there is one feature common to all the varieties, namely, the absence of conspicuous felspar. For the most part, the grit occurs as beds several feet thick, but near the top of the quarry face it is rather flaggy. The base of each bed is a band of conglomerate (called "suet" by the quarryman) six inches to a foot thick; these con-

¹ Crushed in the laboratory.

glomeratic bands are composed of quartzite pebbles, $\frac{1}{2}$ in. or more across, cemented by limonite and decomposed feldspathic matter. In each bed, overlying the conglomeratic base, are several feet of grit, either medium-grained or, more frequently, composed of alternate fine- and coarse-grained layers. Some of this grit contains scattered quartzite pebbles. The grit in some beds is stained a deep ochreous brown; in others it may be faint brown or even white. The top of each bed is usually fine-grained, though in the flaggy beds near the top of the quarry face the grit consists of layers, about $\frac{1}{2}$ in. thick, in which there is a graduation from medium- or even coarse-grained grit to a very fine-grained, almost silty, grit.

A sample of the medium-grained grit from the middle of one of the beds was examined microscopically. The sample was banded in shades of brown. Under the microscope it was seen to consist of angular-to-subangular grains of quartz and a few of feldspar, together with interstitial sericite and kaolin. There were also one or two flakes of muscovite. Limonite occurs in some parts of the slide. Most of the quartz grains are large single ones, up to 0.7 mm. or more across, more or less strained and containing bubble inclusions. Some of them have a skin of secondary silica, separated from the core by a layer of iron oxide. Most of the feldspar is fresh microcline microperthite, though there is some rather decomposed medium plagioclase. The sericite is rather iron-stained. The microstructure of the grit is dominated by quartzitic aggregates, which enclose some of the feldspars. The sericite occurs either as thin films between the quartzitic aggregates or, in association with the kaolin, as interstitial pockets. In some parts of the microsection, thin films of limonite occur along the sutured junctions of the grains in the quartzitic aggregates. There is also some interstitial limonite. A micrometric analysis gave the following results :

Quartz	83.30%
Microcline microperthite and plagioclase	6.03%
Mica (sericite and muscovite)	6.95%
Kaolin	1.12%
Limonite	2.63%
	<hr/> 100.03%

The crushed grit supplied by the quarry will vary considerably in composition according to the beds being worked in the quarry; it is supplied as passing through a $\frac{1}{4}$ -in. mesh rotating sieve after being crushed in an edge-runner mill. The grit contains a large number of composite grains. It was sieved, and that remaining on the 0.25-mm. but passing through the 0.5-mm. mesh was rinsed. This washed fraction was pale brown in mass and composed of sub-angular quartz grains, partially, or in some cases entirely, coated with limonite. Feldspar grains were rare.

Heavy Minerals.—0.80% of heavy minerals was found in a sample of the grit crushed at the quarry. The mineral species identified were :

Zircon : Very abundant; prismatic with well-rounded pyramids.

Rutile : Frequent; dark-red irregular grains.

Fluorspar : Frequent; colourless-to-violet cleavage fragments.

Monazite : Very rare; yellow squares with dark borders.

Magnetite : Frequent; opaque silvery grains.

Ilmenite : Frequent; opaque grey grains, partly altered to leucoxene.

S5, Upper Burbage Grit. *Houndkirk Quarry, near Ringinglow.*

Locality.—By the old road from Ringinglow to Fox House, $\frac{1}{2}$ mile south-west of Ringinglow.

Owner.—Mr. J. Keeling, 258 Dobbin Hill, Sheffield, 11.

Petrological Description.

This grit sample was collected from the weathered zone, about 4 ft. thick, at the top of the quarry face. It is a pale-brown, medium-grained grit, containing a few scattered quartzite pebbles, up to $\frac{1}{2}$ in. in dia. There are a few thin layers of conglomerate composed of quartzite and felspar pebbles set in a fine-grained, rather limonitic matrix.

Microscopic examination of the weathered grit shows that it is not very felspathic; it consists of quartz, felspar and sericite, together with a little limonite and kaolin. The quartz grains are subangular and of two distinct grain sizes; there are many large grains 1.0–1.2 mm. across and numerous small grains less than 0.3 mm. across. Some of these small grains may form composite grains. Most of the quartz is free from strain and is crossed by many lines of bubbles. The felspar is nearly all microcline microperthite; only one or two grains of plagioclase were found. The felspar cleavages are unusually well developed, and sericitisation of the microcline is more advanced than in most grits. The sericite is iron-stained.

The microstructure is characterised by quartzitic aggregates composed of large and small grains intricately sutured together. Many of the felspars are enclosed in the quartzitic aggregates. The sericite, kaolin and limonite are interstitial to the quartz and felspar.

A micrometric analysis of the grit gave the following composition:

Quartz	83.22%
Microcline microperthite and plagioclase	7.89%
Mica (sericite and muscovite)	6.98%
Kaolin	0.95%
Limonite	1.02%
	<hr/> 100.06%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5-mm. and 0.25-mm. mesh was tinged with brown. It consisted of angular-to-subangular quartz grains, most of which were partly or wholly coated with limonitic and sericitic matter.

Heavy Minerals.—0.20% of heavy minerals was found in the crushed grit. The mineral species identified were:

Zircon: Very abundant; prismatic with rounded ends.

Rutile: Frequent; dark reddish-brown irregular grains.

Tourmaline: Frequent; rectangular grains, pleochroic in shades of greenish-brown.

Monazite: Rare; yellow rectangular grains.

Garnet: Rare; amethyst-coloured rounded grains of almandine.

Magnetite: Frequent; altering to limonite.

Ilmenite: Frequent; nearly all altered to leucoxene.

S6, Brown Edge Flags. *Brown Edge Quarries, near Ringinglow.*

Locality.—Near the Ringinglow–Hathersage road, $\frac{3}{4}$ mile west-north-west of Ringinglow.

Owner.—Quarry disused.

Petrological Description.

The sample was collected from the weathered tips adjoining the quarries. It is a pale brown, fine-grained sandstone which splits into flags along planes with mica flakes.

Microscopic examination shows that the sandstone consists of quartz and a little felspar and muscovite, together with sericite, limonite and kaolin. The quartz occurs as angular grains, less than 0.30 mm. across, containing few bubble inclusions and being fairly free from strain. The felspar is microcline or, in a few instances, plagioclase; it is decomposing to sericite. There are a few flakes of muscovite. The sericite is iron-stained and merges into patches of limonite. Kaolin fills one or two small pockets. Structurally the rock is composed of quartzitic aggregates in which, in some parts of the slide, adjacent grains are separated by thin films of sericite or limonite. Most of the sericite and limonite is interstitial.

Micrometric analysis gave the following results :

Quartz	85.13%
Microcline and plagioclase	4.19%
Mica (sericite and muscovite)	5.60%
Limonite	5.08%
	<hr/>
	100.00%

The sample was crushed in the laboratory. After washing, the fraction which passed through the 0.5-mm. mesh but remained on the 0.25-mm. mesh was rather brown in mass. It was composed of subangular quartz grains, most of which were coated with sericitic and limonitic matter.

Heavy Minerals.—0.06% of heavy minerals was found in a sample of the crushed rock. The mineral species identified were :

Zircon : Very abundant; prismatic with rounded pyramids.

Rutile : Frequent; yellowish-brown prismatic grains.

Tourmaline : Frequent; intensely pleochroic, ranging from colourless to deep brown or to purplish-brown.

Monazite : Very rare; yellow rectangular grains.

Magnetite : Frequent; coated with limonite.

Ilmenite : Frequent; coated with leucoxene.

S7, Upper Burbage Grit. "Clarion" Quarry, near Ringinglow.

Locality.—On the road from Ringinglow to the Clarion Club House, $\frac{3}{4}$ mile south of Ringinglow.

Owner.—Quarry disused.

Petrological Description.

This sample was collected from the weathered zone, about 5 ft. thick, at the top of the quarry face. The rock is a weathered grit the grain size of which varies from coarse to fine in a thickness of less than an inch. Felspar is not conspicuous. Most of the pieces are pale brown inside and have a deep-brown crust of limonite due to the weathering. Mica flakes occur on some of the bedding planes.

Microscopic examination shows that the grit consists chiefly of quartz grains and a few of felspar, together with sericite and limonite. The quartz occurs as single angular grains the size of which ranges from 1.6 mm. in the coarser bands to less than 0.6 mm. in the finer

bands; most of the grains are free from strain shadows and contain linearly-arranged bubbles. The felspar is fresh microcline. The sericite is iron-stained and merges into opaque patches, which probably consist of limonite and kaolin. Recognisable kaolin is rare.

Though quartzitic aggregates are characteristic of the micro-structure, the suturing of the grains is not so marked as in most grits. The sericite and limonite occur along the junctions between some of the quartz grains, or else interstitially, in some cases in the quartzitic aggregates.

A micrometric analysis gave the following composition :

Quartz	82.94%
Microcline	4.40%
Mica (sericite and muscovite)	8.63%
Limonite with (?) kaolin	4.02%
	<hr/>
	99.99%

The grit was crushed in the laboratory. After washing, the fraction between 0.5-mm. and 0.25-mm. mesh was pale brown in mass. The quartz grains were subangular and many of them were perfectly clean; others were partially coated with limonite. Felspar grains were rare.

Heavy Minerals.—0.18% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon: Very abundant; prismatic with rounded pyramids.

Rutile: Frequent; reddish-brown prismatic or irregular grains; one geniculate twin seen.

Tourmaline: Frequent; pleochroic in shades of greenish brown.

Monazite: Rare; pale-yellow squares.

Garnet: Rare; amethyst-coloured almandine.

Magnetite: Frequent.

Ilmenite: Frequent; partly altered to leucoxene.

S8, Kinderscout Grit. Stoke Quarry, near Grindleford.

Locality.—Near the junction of the roads from Grindleford to Eyam and Calver, $\frac{1}{2}$ mile south-south-west of Grindleford.

Owner.—Stoke Quarry, Ltd., Grindleford.

Petrological Description.

The rock in this quarry varies from a medium-grained arkose in the lower part of the face to a fine-grained, rather micaceous sandstone in the upper part. The grit is pale brown in the lower part of the face and darkens towards the top of the face. The fine-grained sandstone encloses numerous plant remains. Clay and cank-balls¹ are common, particularly in the fine-grained beds. The rock is thick-bedded, almost massive, at the bottom of the face, but towards the top it becomes thin-bedded, almost flaggy, and shale partings appear.

Microscopic examination of the arkose shows that it is composed of quartz and abundant felspar, together with sericite and a little kaolin and limonite. Most of the quartz occurs as large grains up

¹ This term, used by quarrymen, refers to spherical masses of sand bonded together by limonite.

to 1.5 mm. across, though there are some grains about 0.25 mm. across; grains of quartzite are rare. The quartz contains linearly-arranged bubbles and is fairly free from strain. The felspar is not so fresh as in most of the grits examined; it is chiefly microcline, though there is a noteworthy amount of plagioclase. The sericite is iron-stained and is associated with more or less bleached biotite. The latter is an unusual occurrence, the normal primary mica of the grits being muscovite.

The microstructure is characterised by quartzitic aggregates which enclose many of the felspar grains. Sericite, kaolin and limonite occur interstitially both between and in the quartzitic aggregates.

A micrometric analysis of the arkose gave the following results :

Quartz	75.98%
Microcline and plagioclase	14.62%
Mica (sericite and biotite)	7.32%
Kaolin	2.06%
	<hr/> 99.98%

A sample of the crushed grit supplied by the quarry was sieved. After washing, the fraction between 0.5-mm. and 0.25-mm. mesh was pale brown in mass. Most of the quartz grains were sub-angular and clean, though some were slightly coated with limonite. Few felspar grains could be seen. Muscovite flakes were conspicuous as were small grains of limonite.

Heavy Minerals.—0.32% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

- Zircon* : Very abundant; prisms with rounded pyramids.
- Rutile* : Frequent; foxy-red or yellowish-brown prismatic grains.
- Tourmaline* : Frequent; greenish or purplish-brown.
- Fluorspar* : Very rare; cleavage fragments.
- Magnetite* : Frequent; coated with limonite.
- Ilmenite* : Frequent; much leucoxenised.

S9, Upper Burbage Grit. Longshaw Quarry, near Grindleford.

Locality.—Adjoining the Grindleford-Sheffield road, 1½ mile north-east of Grindleford.

Owner.—Messrs. J. E. Nadin & Son, Ltd., Sheffield.

Petrological Description.

The sample was collected from the quarry tip. The rock is a medium- to coarse-grained arkose, which occurs as beds several feet thick; it is a white rock, flecked with brown.

Microscopic examination shows that the grit consists chiefly of quartz and felspar, together with sericite and kaolin. The quartz occurs as large single grains, up to 2 mm. across, traversed by lines of bubbles and more or less strained; some of the grains have skins of secondary silica. The felspar is microcline micropertthite. The sericite is iron-stained. There are one or two flakes of muscovite.

The microstructure is characterised by quartzitic aggregates, which enclose much of the felspar. The sericite and kaolin are interstitial to the quartz and felspar. Some of the sericite occurs as films between the quartz grains.

A micrometric analysis gave the following composition :

Quartz	86.08%
Microcline microperthite	9.12%
Mica (sericite and muscovite)	3.76%
Kaolin	1.06%
								<hr/> 100.02%

The grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was a darker brown than that of the other grits similarly treated. It was composed of sub-angular quartz grains, many of which were partly coated with limonite. Felspar was not abundant.

Heavy Minerals.—0.28% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon : Very abundant; prismatic with rounded pyramids.

Rutile : Frequent; dark-red or yellowish-brown prismatic grains.

Tourmaline : Rare; greenish-brown rectangular grains.

Monazite : Very rare; pale-yellow rounded grains.

Garnet : Very rare; rounded grains of almandine.

Magnetite : Frequent; stained with limonite.

Ilmenite : Frequent; coated with leucoxene.

S10, S11, S12, Kinder Scout Grit. *Birchover, near Bakewell.*

Locality.—A group of three quarries on the east side of Birchover, 4 miles south-east of Bakewell.

Owners.—S10 : Messrs. James Akeroyd & Sons, Ltd. (Lower Quarry), Birchover.

S11 : Messrs. Ann Twyford's Quarry, Stanton-in-the-Peak, near Rowsley.

S12 : Messrs. James Akeroyd & Sons, Ltd. (Upper Quarry), Birchover.

Petrological Description.

The rock at all three quarries is a medium-grained arkose the colour of which varies in bands from pink to pale brown. S10 and S11 are fairly uniform in grain size, but S12 is rather coarser and contains small pebbles. In the Lower Quarry and in the lower part of the other two quarries the rock occurs in beds several feet thick, which are worked for freestone. Alternating layers of sandstone and shale overlie the freestone at the latter two quarries.

Microscopic examination shows that these arkoses contain an unusually high proportion of kaolin. They are composed of quartz, felspar, sericite and kaolin. Quartz grains are angular, rarely composite, and enclose bubbles which, in most cases, are linearly arranged; the grains are about 0.5 mm. across, though S12 contains some grains 3 mm. across. Most of the felspar is fresh microcline microperthite, though there is some rather sericitised plagioclase—particularly in S10. Though the mica is chiefly iron-stained sericite, there is an appreciable quantity of more or less bleached biotite. Flakes of muscovite are not uncommon. The kaolin shows a well-developed vermicular structure. There are a few patches of calcite.

Quartzitic aggregates are not so well developed as in many of

the grits. Many of the quartz grains are separated by mica or kaolin. Most of the sericite and kaolin is interstitial.

Micrometric analysis gave the following results :

	S10.	S11.	S12.
Quartz	78·07%	77·82%	79·49%
Felspar	11·43%	10·58%	12·86%
Mica	4·13%	4·84%	3·69%
Kaolin	6·38%	6·76%	3·96%
	100·01%	100·00%	100·00%

Samples of the rocks were crushed in the laboratory. The fractions between 0·5 mm. and 0·25 mm., after washing, were very similar. Nearly all the quartz grains were subangular and free from limonite; the colour in mass was faintly pink or brown. There was a noteworthy amount of felspar, and muscovite flakes were conspicuous.

Heavy Minerals.—The following heavy minerals were found in samples of the crushed grits :

	S10.	S11.	S12.
<i>Pink almandine garnet</i> . .	Very abundant	Very abundant	Very abundant
<i>Brown tourmaline</i>	Frequent	Frequent	Frequent
<i>Zircon</i> . .	Frequent	Rare	Frequent
<i>Rutile</i> . .	Frequent	Frequent	Frequent
<i>Magnetite</i> . .	Very frequent	Very frequent	Frequent
<i>Ilmenite</i> . .	Frequent	Frequent	Frequent
Total amount	0·12%	0·12%	0·07%

S13, Kinder Scout Grit. *Stancliffe Quarry, Darley Dale.*

Locality.—Adjoining the main road at Darley Dale near Matlock.

Owner.—Stancliffe Estates Co., Darley Dale, near Matlock.

Petrological Description.

This rock is a medium-grained arkose, for the most part pale brown in colour, but occasionally white or reddish-brown. Some of the beds contain quartzite pebbles up to $\frac{1}{4}$ in. across. Flakes of muscovite occur throughout the beds.

Microscopic examination shows that the rock is extremely felspathic. It is composed of quartz, felspar, mica and kaolin. The quartz grains are angular and mostly about 0·5 mm. across, though grains up to 1·3 mm. across do occur. Composite grains are not uncommon. Most of the quartz grains enclose linearly arranged bubbles, and some have skins of secondary silica. The felspar is chiefly fresh microcline micropertite, though there is some sericitised plagioclase. The mica is iron-stained sericite and more or less decomposed biotite; the latter is remarkably abundant. There are a few flakes of muscovite. The kaolin is more finely divided than in the Kinder Scout Grit from Birchover (S10, S11, and S12). There is a little calcite.

The microstructure is characterised by well-sutured quartzitic aggregates separated by rather large patches of mica and kaolin. Very little mica or kaolin is enclosed in the quartzitic aggregates.

A micrometric analysis of the grit gave the following results :

Quartz	72.85%
Microcline and plagioclase	15.77%
Mica	6.54%
Kaolin	4.87%

100.03%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was pale brown in mass. It was composed of subangular quartz grains, some of which were partly coated with limonite. Felspar and muscovite were conspicuous.

Heavy Minerals.—0.14% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Almandine garnet: Very abundant.

Rutile (red-brown): Frequent.

Tourmaline (green-brown): Frequent.

Zircon: Frequent.

Magnetite with limonite: Frequent.

Ilmenite with leucoxene: Abundant.

S14, Kinderscout Grit. *Black Rocks Scree, near Cromford.*

Locality.—Adjoining the High Peak Mineral Railway, 1 mile south of Cromford.

Owner.—Quarry disused.

Petrological Description.

This sample was collected from a small quarry at the foot of the scree. The rock is a medium- or coarse-grained arkose, often pebbly. The colour depends on the degree of weathering; most of the rock is only speckled with brown, but some is stained a deep reddish-brown.

Microscopic examination shows that the arkose consists essentially of quartz, felspar, mica and kaolin, together with some hematite and limonite. The quartz is subangular, rarely composite, and contains some scattered bubble inclusions; most of the grains are less than 0.5 mm. across, though there are a number of large grains over 1.5 mm. across. The felspar grains are rounded and are almost all microcline micropertthite showing little or no sign of alteration, although the weathering has made the rock quite crumbly. Much of the mica is iron-stained sericite and is associated with patches of limonite. There are a few flakes of muscovite. The kaolin shows a typical vermicular structure. Patches of calcite are not uncommon.

Quartzitic aggregates are poorly developed. Although the quartz grains are sutured together, dovetailing is rare. The mica and kaolin occur along the junctions of the quartz grains or in interstitial pockets.

A micrometric analysis gave the following composition :

Quartz	80.24%
Microcline micropertthite	10.10%
Mica	4.58%
Kaolin	3.42%
Hematite and limonite	1.66%

100.00%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was reddish-brown in mass. It was composed of subangular quartz grains, many of which were partly coated with hematite. Felspar was conspicuous. There were a few flakes of muscovite.

Heavy Minerals.—0.08% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

<i>Almandine garnet</i> : Very abundant.	<i>Zircon</i> : Rare.
<i>Rutile (red-brown)</i> : Frequent.	<i>Limonite</i> : Frequent.
<i>Tourmaline (green-brown)</i> : Frequent.	<i>Ilmenite and leucozene</i> : Frequent.

S15, Kinderscout Grit. *Shire Hill Quarry, near Glossop.*

Locality.—Adjoining the Sheffield-Ashopton-Manchester road, 1 mile east of Glossop.

Owner.—Mr. J. Greenwood, Glossop.

Petrological Description.

The rock at this quarry is a coarse-grained, rather felspathic grit, which occurs as thick beds. The fresh grit is pale grey, but near bedding planes and joints it has changed to pale brown.

Microscopic examination shows that the grit consists of quartz, felspar and sericite, together with a little muscovite and kaolin. The quartz occurs as angular grains, rarely composite, less than 0.8 mm. across, though there are a few grains over 2 mm. across. Linearly-arranged bubbles are uncommon. The felspar is nearly all fresh microcline micropertthite which forms rounded grains. The sericite is rather iron-stained and is associated with limonite. There are one or two flakes of decomposed biotite. There is a little calcite.

The microstructure is characterised by quartzitic aggregates in which many of the grains are separated by thin films of sericite. The kaolin, limonite and some of the sericite occur interstitially.

A micrometric analysis gave the following results :

Quartz	82.35%
Microcline micropertthite	9.16%
Mica	8.23%
Kaolin	0.24%
							<hr/> 99.98%

A sample of the crushed grit supplied by the quarry was sieved and washed. The fraction between 0.5 mm. and 0.25 mm. was pale brown in mass. It was composed of subangular quartz grains, most of which were partly coated with clayey matter and limonite. There were some felspar grains and a few flakes of muscovite.

Heavy Minerals.—0.08% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

<i>Almandine garnet</i> : Very abundant.	<i>Magnetite</i> : Frequent.
<i>Rutile (red-brown)</i> : Frequent.	<i>Limonite</i> : Frequent.
<i>Zircon</i> : Frequent.	<i>Ilmenite and leucozene</i> : Abundant.
<i>Tourmaline (green-brown)</i> : Rare.	

S16, Kinderscout Grit. *Ladybower Quarry, west of Sheffield.*

Locality.—Adjoining the Sheffield-Ashopton-Manchester road, just east of Ladybower Village.

Owner.—Mr. J. Greenwood, Glossop.

Petrological Description.

This rock is a coarse-grained pebbly arkose, which is pale grey when fresh. The joints and bedding planes are frequent, and near them the rock has altered to pale brown. Thin bands of conglomerate are not uncommon.

Microscopic examination shows that the arkose consists of quartz, felspar and mica, together with a little kaolin and limonite. The quartz grains vary considerably in size; most of them are less than 0.6 mm. across, though some are as much as 4 mm. across. Composite grains are not uncommon. Most of the grains contain linearly-arranged bubbles. The felspar is microcline microperthite, for the most part slightly sericitised along the cleavage planes. The mica is mostly iron-stained sericite which merges into patches of limonite. Flakes of muscovite are rare. There is a little calcite.

The microstructure is characterised by quartzitic aggregates. Though some of the sericite occurs along the junctions between the quartz grains, most of it, like the kaolin and limonite, is interstitial.

A micrometric analysis gave the following composition :

Quartz	77.67%
Microcline microperthite	11.66%
Mica	9.87%
Limonite	0.77%
						<hr/>
						99.97%

A sample was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was pale brown in mass. It was composed of subangular quartz grains, a few of which were slightly coated with limonite. Felspar grains were common. There were one or two flakes of muscovite.

Heavy Minerals.—0.15% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

<i>Almandine garnet</i> : Very abundant.	<i>Zircon</i> : Frequent.
<i>Rutile (red-brown)</i> : Frequent.	<i>Magnetite</i> : Frequent.
<i>Tourmaline (green-brown)</i> : Frequent.	<i>Limonite</i> : Abundant.
	<i>Ilmenite and leucozene</i> : Abundant.

S17, Rough Rock. *Alton Quarry, near Clay Cross.*

Locality.—In Alton village, 2 miles west-north-west of Clay Cross.

Owner.—Mr. Henry Hopkinson, Alton, near Chesterfield.

Petrological Description.

In this quarry the lower beds are composed of medium-grained freestone containing little felspar, while the upper beds are micaceous flags. Some of the freestone beds are separated by flaggy partings. Samples of the freestone were collected from the tip; the weathering produces speckles of brown limonite.

Microscopic examination shows that the freestone from the tip consists of quartz, felspar, mica and kaolin. The quartz is remark-

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was a faint purplish-grey in mass. It was composed of subangular quartz grains, some of which were partly coated with limonite. There was some carbonaceous matter. Felspar grains were conspicuous.

Heavy Minerals.—0.14% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were:

Zircon: Abundant.

Almandine garnet: Rare.

Rutile (red-brown): Frequent.

Limonite: Abundant.

Tourmaline (green-brown): Frequent.

Leucozene: Abundant.

S19, Chatsworth Grit. *Beeley Moor, near Chatsworth Park.*

Locality.—Adjoining the road from Holymoorside to Beeley, 1 mile east of Beeley.

Owner.—Quarry disused.

Petrological Description.

This sample was collected from the subsoil, 3 ft. thick, which is of podsol type. The partly-weathered rock is a fine-grained grit faintly tinged with brown.

Microscopic examination shows that the grit consists of quartz, felspar, mica and kaolin, together with a little limonite. The quartz is remarkably even-grained, the grain size being about 0.25 mm. The quartz encloses scattered bubble inclusions. Some of the grains have skins of secondary silica. No composite grains were noticed. The felspar is fresh microcline. Most of the mica is iron-stained sericite, though there are a few flakes of muscovite.

The microstructure is characterised by quartzitic aggregates separated by patches of sericite and kaolin. The quartz grains are more or less dovetailed together.

A micrometric analysis gave the following results:

Quartz	82.08%
Microcline	4.06%
Mica	8.56%
Kaolin	4.25%
Limonite	1.04%
						<hr/>
						99.99%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was grey-brown in mass. It was composed of subangular-to-rounded quartz grains, only slightly coated with limonite. It contained many small aggregates of limonitic matter. There were a few felspar grains and muscovite flakes.

Heavy Minerals.—0.07% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were:

Zircon: Very abundant.

Limonite: Abundant.

Rutile (red-brown): Frequent.

Leucozene: Abundant.

Rutile (yellow-brown): Frequent.

Tourmaline (brown): Rare.

S20, S23, Wingfield Flags. *West of Chesterfield.*

Localities.—S20: Bole Hill, Press, 3 miles south-south-west of Chesterfield.

S23: Freebitch, 4 miles west of Chesterfield.

Owners.—S20 : Mr. P. Gregory, Darley Dale.

S23 : Mr. H. White, Freebitch, Eastmoor.

Petrological Description.

The rock from both the localities is a silty flagstone. The sample from Bole Hill is more weathered than that from Freebitch. As the weathering proceeds, the colour of the rock changes from greenish-grey to brown. Both samples show the false-bedding characteristic of siltstones; the bedding planes are covered with mica flakes. The rock at both localities has been extensively quarried for building stone and is referred to in the trade as "delft." Under the microscope both rocks are seen to consist of quartz, a little felspar and abundant mica, together with a little kaolin.

The quartz occurs as angular grains, remarkably uniform in size—usually about 0.10 mm. across; the inclusions are not linearly arranged. Many of the quartz grains show signs of secondary silicification. The felspar is microcline, together with a few grains of plagioclase, and is slightly decomposed. The mica is muscovite and sericite; the latter is rather iron-stained, especially so in S20.

The microstructure is characterised by quartzitic aggregates separated by extensive patches of sericite and kaolin. The quartz grains are closely sutured together.

Micrometric analysis of the rocks is difficult, owing to their fine grain. The analyses are :

	S20.	S23.
Quartz	71.42%	69.84%
Felspar	6.45%	5.99%
Mica	20.28%	22.20%
Kaolin	1.87%	2.01%
	100.02%	100.04%

Samples of the rocks were crushed in the laboratory. The rocks are so fine-grained that the fraction between 0.5 mm. and 0.25 mm. is composed of composite grains differing but little from the original rocks.

Heavy Minerals.—The following heavy minerals were found in samples of the crushed grits :

	S20.	S23.
<i>Almandine garnet</i>	Rare
<i>Rutile (red)</i>	Frequent	Frequent
<i>Tourmaline (brown)</i>	Rare	Very rare
<i>Zircon</i>	Very abundant	Abundant
<i>Magnetite</i>	Frequent	Frequent
<i>Limonite</i>	Frequent	Abundant
<i>Ilmenite</i>	Abundant	Frequent
<i>Leucozene</i>	Abundant	Abundant
Total amount	0.06%	0.06%

S21, Rough Rock. Red Lion Inn, near Chesterfield.

Locality.—On the main road from Chesterfield to Darley Dale, 4 miles south-west of Chesterfield.

Owner.—Quarry disused.

Petrological Description.

Most of the rock in this quarry is a white, medium- to coarse-grained, feldspathic grit which occurs as massive beds. One or two thin beds contain an appreciable quantity of iron oxide and have weathered to a dark-red colour; these beds were not included in the sample.

The white grit is composed of quartz, feldspar, sericite and kaolin. The quartz grains are angular and of fairly uniform size, about 0.60 mm. across, though some are as much as 0.90 mm. across. There are several fine-grained bands in the section. The quartz grains contain inclusions often linearly arranged, and many of them are coated with secondary silica. The feldspar is fresh microcline microperthite. The sericite is but slightly iron-stained. The kaolin shows well-developed vermicular structure on a rather coarse scale.

The microstructure is characterised by quartzitic aggregates in which the quartz grains are intricately sutured together. These aggregates enclose most of the feldspar. The sericite and kaolin are interstitial.

A micrometric analysis of the grit gave the following results :

Quartz	79.84%
Microcline microperthite	9.72%
Sericite	6.12%
Kaolin	4.31%
						<hr/>
						99.99%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was pale brown in mass. It was composed chiefly of clean, subangular quartz grains, only a few grains being slightly coated with limonite. There were one or two grains of opaque feldspar.

Heavy Minerals.—0.08% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon : Frequent.

Rutile (red-brown) : Frequent.

Tourmaline (green-brown) : Frequent.

Limonite : Abundant.

Leucozene : Abundant.

S22, Chatsworth Grit. *Roaches Quarry, Stone Edge.*

Locality.—Adjoining the main road from Chesterfield to Darley Dale, 5 miles south-west of Chesterfield.

Owner.—Messrs. Durhills, Sandiron House, Beauchief, Sheffield.

Petrological Description.

The rock in this quarry is a rather feldspathic, brown grit which varies considerably in grain size. It occurs as thick beds and is rather weathered.

It is composed of quartz, feldspar, mica and kaolin. The quartz occurs as angular-to-subangular grains, which are traversed by many lines of bubble inclusions. Secondary silicification of the quartz grains is not uncommon. The feldspar is fresh microcline microperthite, with well-developed cleavage cracks. The mica is of three types; besides a few flakes of muscovite and the usual aggregates of sericite, there is a considerable amount of a brown pleochroic ferromagnesian mica

showing zonary structures. The kaolin has the typical vermicular structure.

The microstructure is characterised by quartzitic aggregates which enclose much of the felspar. The quartz grains are not dovetailed together. The mica and kaolin are interstitial to the quartzitic aggregates.

The coarse-grained grit contains less mica and kaolin than the fine-grained variety. A micrometric analysis of the coarse grit gave the following results :

Quartz	84.35%
Microcline micropertthite	6.55%
Mica	6.68%
Kaolin	2.44%
						<hr/>
						100.02%

A sample of the grit was crushed in the laboratory. The fraction between 0.5 mm. and 0.25 mm. was brown in mass after washing. It was composed of subangular quartz grains, more or less coated with limonitic matter. There were a few opaque grains of felspar.

Heavy Minerals.—0.07% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon : Abundant.

Rutile (red-brown) : Abundant.

Rutile (yellow-brown) : Abundant.

Tourmaline (green-brown) : Frequent.

Magnetite : Frequent.

Limonite : Abundant.

Ilmenite : Frequent.

Leucozene : Abundant.

S24, Grenoside Rock. Wortley Stone Quarries.

Locality.—Adjoining the Thurgoland-Stocksbridge road, 1 mile south of Thurgoland.

Owner.—Wortley Stone Quarries, Ltd., near Stocksbridge.

Petrological Description.

This is a pale-brown, felspathic grit, which weathers to a deep brown. Some of the bedding planes are covered with plant remains and flakes of muscovite.

The grit is composed of quartz, felspar, mica and kaolin. Quartz grains are angular, usually 0.3–0.5 mm. across, though some are as much as 0.9 mm. across; most of the grains enclose linearly-arranged inclusions. Many of the grains have coats of secondary silica. The felspar is fresh microcline micropertthite and occurs as rounded grains. The mica is mainly iron-stained sericite, though there are a few flakes of muscovite.

The microstructure is characterised by quartzitic aggregates which enclose much of the felspar. The kaolin and mica lie between the aggregates.

A micrometric analysis of the grit gave the following results :

Quartz	76.63%
Microcline micropertthite	10.85%
Mica	6.13%
Kaolin	6.38%
						<hr/>
						99.99%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was a pale greenish-brown in mass. The quartz grains were angular-to-subangular, and a few of them were partly coated with limonitic matter. A little opaque feldspar, some muscovite and a few aggregates of the matrix were also present.

Heavy Minerals.—0.06% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Almandine garnet : Very abundant.

Zircon : Frequent.

Rutile (red-brown) : Frequent.

Rutile (yellow-brown) : Frequent.

Tourmaline (green-brown) : Rare.

Monazite : Very rare.

Magnetite : Frequent.

Limonite : Abundant.

Ilmenite : Frequent.

Leucoxene : Abundant.

S25, Greenmoor Rock. *Greenmoor Quarry, near Stocksbridge.*

Locality.—In Greenmoor village, 1 mile north of Stocksbridge.

Owner.—Quarry disused.

Petrological Description.

This is a fine-grained siltstone showing small-scale false-bedding, in which the bedding planes are covered with carbonaceous matter and muscovite flakes.

The rock is composed of quartz, feldspar, sericite and kaolin. The quartz occurs as angular grains of uniform size, mostly 0.10 mm. across; inclusions are common. Some of the grains have coats of secondary silica. The feldspar is nearly all fresh microcline microperthite, though there are a few grains of rather decomposed plagioclase. The matrix or bond is extremely fine-grained; it consists of kaolin and sericite, the latter deeply stained with limonite.

The microstructure is characterised by small quartzitic aggregates completely surrounded by the matrix of sericite and kaolin.

In the following micrometric analysis the sericite and kaolin are grouped together, as they are too fine-grained to be separated in the analysis :

Quartz	51.52%
Feldspar	6.12%
Matrix	42.35%
						<hr/> 99.99%

A sample of the rock was crushed in the laboratory. The fraction between 0.5 mm. and 0.25 mm. was composed entirely of composite grains differing but little in appearance from the original rock.

Heavy Minerals.—0.06% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

Zircon : Very abundant.

Almandine garnet : Rare.

Limonite : Very abundant.

Leucoxene : Very abundant.

S26, Rough Rock. *Hazlehead.*

Locality.—On the main road from Langsett to Huddersfield, $\frac{1}{2}$ mile south of Hazlehead Bridge Station.

Owner.—Quarry disused.

Petrological Description.

The rock sample was collected from the weathered débris in the quarry. The rock is a more or less iron-stained felspathic grit, though some of it has been thoroughly leached to a pale grey colour.

The grit is composed of quartz, felspar, sericite and kaolin. The quartz grains are angular, cracked and traversed by lines of bubble inclusions. Most of the grains are about 0.5 mm. across, though some are nearly 1.0 mm. across. The felspar is microcline microperthite and is slightly decomposed. The sericite is deeply iron-stained.

The microstructure is characterised by extensive quartzitic aggregates in which the quartz is intricately sutured together. Most of the felspar, sericite and kaolin occur between the aggregates.

A micrometric analysis of the grit gave the following results :

Quartz	75.51%
Microcline microperthite	7.34%
Mica	13.04%
Kaolin	4.12%
		<hr/>
		100.01%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was brown in mass. It was composed of angular quartz grains more or less coated with limonitic matter. There were a few flakes of mica and one or two grains of opaque felspar.

Heavy Minerals.—0.06% of heavy minerals was found in a sample of the crushed grit. The mineral species identified were :

<i>Almandine garnet</i> : Abundant.	<i>Magnetite</i> : Frequent.
<i>Zircon</i> : Frequent.	<i>Limonite</i> : Abundant.
<i>Rutile (red-brown)</i> : Frequent.	<i>Ilmenite</i> : Abundant.
<i>Tourmaline (green-brown)</i> : Rare.	<i>Leucoxene</i> : Abundant.

S27, Huddersfield White Rock. Langsett Moors.

Locality.—Roadside exposure, 2 miles west of the Flouch Inn.

Petrological Description.

This is a fine-grained sandstone, slightly stained with limonite. It is rather flaggy, and the bedding planes are covered with flakes of muscovite.

The rock is composed of quartz, felspar, mica and kaolin. The quartz occurs as angular grains, 0.15–0.20 mm. across, occasionally up to 0.40 mm. across. Many of the grains are coated with secondary silica. Scattered bubble inclusions are not uncommon. Flakes of muscovite, more or less distorted, occur in well-defined layers. Kaolin and iron-stained sericite are present in intimate mixture. The felspar is microcline microperthite.

The microstructure is characterised by extensive quartzitic aggregates which enclose most of the felspar. The sericite and kaolin are interstitial to the aggregates. The muscovite is confined to the bedding planes.

The micrometric analysis shows that the sandstone varies in composition from layer to layer. The following two analyses are of two adjacent layers separated by a micaceous bedding plane :

	(a).	(b).
Quartz	73.58%	81.17%
Microcline microperthite	10.35%	3.25%
Matrix	16.10%	15.59%
	<hr/> 100.03%	<hr/> 100.01%

A sample of the rock was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was pale brown in mass and was composed almost entirely of composite grains.

Heavy Minerals.—0.04% of heavy minerals was found in a sample of the crushed grit. / The mineral species identified were :

Zircon : Very abundant.

Rutile (red-brown) : Frequent.

Almandine garnet : Rare.

Tourmaline (green-brown) : Very rare.

Limonite : Very abundant.

Leucoxene : Very abundant.

S28, S29, Rivelin Grit. Rivelin Glen, near Malin Bridge.

Locality.—Two quarries adjoining the main road by the River Rivelin, 1½ mile south-west of Malin Bridge.

Owners.—S28: Messrs. Henry Gosney & Sons, Rivelin Glen Quarries, Sheffield.

S29 : Disused quarry owned by Sheffield Corporation.

Petrological Description.

The rock at these localities is a white-to-brown, coarse-grained arkose. It occurs as thick beds and is worked for freestone.

The rock is composed of quartz, felspar, mica and kaolin. The quartz forms angular-to-subangular grains, up to 2 mm. across, traversed by numerous lines of bubbles. Secondary silicification of the quartz grains is conspicuous. There are some quartzite grains. The felspar occurs as rounded grains composed chiefly of fresh microcline microperthite, though there is a little decomposed plagioclase. With the exception of one or two flakes of muscovite, the mica is sericite, faintly stained with limonite. The kaolin has a coarse vermicular structure.

The microstructure is characterised by extensive quartzitic aggregates which enclose most of the felspar. The quartz grains are intricately sutured together. Nearly all the sericite and kaolin is interstitial to the aggregates.

Micrometric analyses of the grits from the two localities gave the following results :

	S28.	S29.
Quartz	76.38%	78.11%
Felspar	14.73%	12.14%
Mica	4.99%	4.04%
Kaolin	3.92%	5.68%
	<hr/> 100.02%	<hr/> 99.97%

Samples of the grits were crushed in the laboratory. After washing, the fractions between 0.5 mm. and 0.25 mm. were pale brown in mass. They were composed of subangular grains of quartz, a few of which were slightly coated with limonite. There were a few muscovite flakes and some opaque grains of felspar.

Heavy Minerals.—The following heavy minerals were found in samples of the crushed grits :

	S28.	S29.
<i>Pink almandine garnet</i>	Frequent	Abundant
<i>Brown tourmaline</i>	Rare	Frequent
<i>Zircon</i>	Frequent	Frequent
<i>Rutile</i>	Frequent	Frequent
<i>Magnetite</i>	Frequent	Frequent
<i>Ilmenite</i>	Frequent	Frequent
<i>Leucoxene</i>	Frequent	Frequent
Total amount	0.18%	0.12%

The zircon in S28 forms rounded grains, but that in S29 occurs as idiomorphic grains.

S30, Loxley Edge Rock. *East of Bolsterstone.*

Locality.—Disused quarry on the summit of Allman Well Hill, 1 mile east of Bolsterstone.

Owner.—Quarry disused.

Petrological Description.

This rock was once worked extensively for "fire-stone." It is a brown, medium-grained grit containing little felspar, and forms rather massive beds.

The grit is composed of quartz, a little felspar, some sericite and kaolin. The quartz occurs as angular grains, mostly less than 0.5 mm. across, though a few are as much as 1 mm. across. They contain bubble inclusions which are linearly arranged. Some of the grains show signs of secondary silicification. The felspar is rather decomposed microcline micropertthite. The sericite is iron-stained.

The microstructure is that of a quartzite containing small interstitial pockets of sericite and kaolin. The quartz grains are intricately sutured together.

A micrometric analysis gave the following results :

Quartz	92.19%
Microcline micropertthite	1.33%
Sericite	3.00%
Kaolin	3.54%
	<hr/> 100.06%

A sample of the grit was crushed in the laboratory. After washing, the fraction between 0.5 mm. and 0.25 mm. was pale brown in mass. It was composed of subangular quartz grains, only slightly coated with limonite.

Heavy Minerals.—0.04% of heavy minerals was found in a sample of the crushed rock. The mineral species identified were :

Zircon : Frequent.

Brown tourmaline : Frequent.

Rutile : Frequent.

Magnetite : Frequent.

Ilmenite : Frequent.

Leucoxene : Frequent.

APPENDIX B. *The Chemical Compositions of the Rocks.*

The proportions of the minerals in the rocks were determined by means of a traversing micrometric stage; from a knowledge of the chemical compositions of the several minerals, the chemical compositions of the rocks were calculated, and these are recorded in Table VIII. The assumed chemical compositions of the constituent minerals used in

TABLE VIII.—*The Chemical Compositions of the Rocks as Calculated from their Micrometric Analyses.*

	S1.	S2.	S3.	S3W.	S4.	S5.	S6.	S7.
SiO ₂ . % . . .	94.59	89.86	91.13	Not determined as kaolin and limonite could not be measured separately.	90.95	92.04	90.49	89.84
Al ₂ O ₃ . % . . .	3.29	6.48	5.70		4.18	4.46	2.83	4.00
Fe ₂ O ₃ . % . . .	0.02	0.04	0.03		2.29	0.90	4.38	3.47
FeO. %	0.02	0.04	0.03		0.03	0.03	0.03	0.04
MgO. %	0.02	0.04	0.03		0.03	0.03	0.03	0.04
CaO. %	0.02	0.04	0.03		0.03	0.03	0.03	0.04
K ₂ O. %	1.58	2.28	2.05		1.37	1.62	1.01	1.28
Na ₂ O. %	0.27	0.44	0.36		0.25	0.29	0.18	0.24
H ₂ O. %	0.24	0.72	0.69		0.90	0.64	1.00	1.02
Total. % . . .	100.05	99.94	100.05		100.03	100.04	99.98	99.97
	S8.	S9.	S10.	S11.	S12.	S13.	S14.	S15.
SiO ₂ . %	89.79	94.22	90.02	89.71	91.23	88.16	90.34	92.29
Al ₂ O ₃ . % . . .	6.34	3.56	6.59	6.88	5.58	7.56	5.14	4.81
Fe ₂ O ₃ . % . . .	0.04	0.02	0.02	0.02	0.02	0.03	1.44	0.04
FeO. %	0.04	0.02	0.02	0.02	0.02	0.03	0.02	0.04
MgO. %	0.04	0.02	0.02	0.02	0.02	0.03	0.02	0.04
CaO. %	0.04	0.02	0.02	0.02	0.02	0.03	0.02	0.04
K ₂ O. %	2.53	1.52	1.98	1.83	2.05	2.66	1.74	1.90
Na ₂ O. %	0.45	0.26	0.32	0.32	0.35	0.46	0.30	0.35
H ₂ O. %	0.66	0.34	1.10	1.19	0.74	1.02	0.96	0.45
Total. % . . .	99.93	99.98	100.09	100.01	100.03	99.98	99.98	99.96
	S16.	S17.	S18.	S19.	S20.	S21.	S22.	S23.
SiO ₂ . %	89.91	91.24	91.45	90.42	85.84	90.79	92.74	84.93
Al ₂ O ₃ . % . . .	5.77	6.09	5.48	5.88	9.49	6.03	4.79	10.16
Fe ₂ O ₃ . % . . .	0.71	0.02	0.04	0.93	0.11	0.03	0.03	0.11
FeO. %	0.05	0.02	0.04	0.04	0.11	0.03	0.03	0.11
MgO. %	0.05	0.02	0.04	0.04	0.11	0.03	0.03	0.11
CaO. %	0.05	0.02	0.04	0.04	0.11	0.03	0.03	0.11
K ₂ O. %	2.38	1.09	1.85	1.23	2.48	1.80	1.41	2.56
Na ₂ O. %	0.44	0.20	0.33	0.24	0.50	0.32	0.26	0.52
H ₂ O. %	0.62	1.27	0.69	1.18	1.31	0.92	0.68	1.37
Total. % . . .	99.98	99.97	99.96	100.00	100.04	99.98	100.00	99.98
	S24.	S25.	S26.	S27(a).	S27(b).	S28.	S29.	S30.
SiO ₂ . %	89.12	Bond cannot be separated into constituents.	88.00	Bond cannot be separated into constituents.		89.90	90.22	95.85
Al ₂ O ₃ . % . . .	7.22		8.03			6.38	6.38	2.99
Fe ₂ O ₃ . % . . .	0.03		0.07			0.03	0.02	0.02
FeO. %	0.03		0.07			0.03	0.02	0.02
MgO. %	0.03		0.06			0.03	0.02	0.01
CaO. %	0.03		0.06			0.03	0.02	0.01
K ₂ O. %	1.95		2.02			2.40	1.98	0.42
Na ₂ O. %	0.35		0.39			0.40	0.34	0.08
H ₂ O. %	1.21		1.25			0.81	1.00	0.64
Total. % . . .	99.97		99.95			100.01	100.00	100.04

the calculation are shown in Table IX. The felspar composition was determined optically. Sericite is similar in composition to the primary mica muscovite, but contains less potash and more hydroxyl; the chemical composition employed is that of a sericite optically similar to that in the rocks examined. The kaolin was shown by Mr. W. J. Wilde to have the same X-ray pattern as china clay, that is, it is kaolin in the strict sense. The limonite is assumed to have the formula $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

The iron content in all cases is a minimum value only. The determination of iron by micrometric analysis is not very accurate, as in the siltstones, for example, the limonite and kaolin are too closely associated

TABLE IX.—*The Chemical Compositions of the Constituent Minerals of the Rocks.*

	Quartz.	Felspar (80% Micro- cline, 20% Plagioclase).	Sericite.	Kaolin.	Limonite.
SiO ₂ . % .	100.00	65.60	46.51	39.60	...
Al ₂ O ₃ . %	18.55	36.58	46.40	...
Fe ₂ O ₃ . %	0.51	...	85.50
FeO. %	0.48
MgO. %	0.46
CaO. %	0.44
K ₂ O. %	13.65	7.84
Na ₂ O. %	2.18	1.77
H ₂ O. %	5.14	13.95	14.50
Total. % .	100.00	99.98	99.73	99.95	100.00

for separate measurements to be made, and in most of the rocks the quartz grains are iron-stained and sometimes have a limonite coating.

Comparisons of the chemical and micrometric analyses for eight of the rocks, and a chemical analysis of S25 (Greenmoor Rock), which could not be examined micrometrically, are given in Table X.

TABLE X.—*Comparisons of Chemical and Micrometric Analyses.*

	S2.		S3. Unweathered.		S4.		S18.		S19.	
	Chemical.	Micrometric.	Chemical.	Micrometric.	Chemical.	Micrometric.	Chemical.	Micrometric.	Chemical.	Micrometric.
SiO ₂ . % .	90.15	89.86	88.53	91.13	89.35	90.95	88.03	91.45	87.17	90.42
Al ₂ O ₃ . %	6.72	5.70	4.39	4.18	6.95	5.48	6.34	5.88
Fe ₂ O ₃ . %	0.74	0.03	2.68	2.29	0.78	0.04	1.64	0.93
FeO. %	N.d.	0.03	N.d.	0.03	N.d.	0.04	N.d.	0.04
TiO ₂ . %	0.16	N.d.	0.24	N.d.	0.29	N.d.	0.35	N.d.
CaO. %	0.12	0.03	0.12	0.03	0.08	0.04	0.09	0.04
MgO. %	0.24	0.03	0.31	0.03	0.28	0.04	0.24	0.04
K ₂ O. %	1.86	2.05	1.21	1.37	2.10	1.85	1.41	1.23
Na ₂ O. %	0.62	0.36	0.54	0.25	0.41	0.33	0.34	0.24
H ₂ O. %	0.95	0.69	1.08	0.90	1.02	0.69	1.46	1.18
Total. % .	90.15	89.86	99.94	100.05	99.92	100.03	99.94	99.96	100.04	100.00

	S21.		S24.		S25.	S28.		S30.	
	Chemical.	Micrometric.	Chemical.	Micrometric.	Chemical.	Chemical.	Micrometric.	Chemical.	Micrometric.
SiO ₂ . % .	89.11	90.79	86.75	89.12	75.03	87.77	89.90	94.05	95.85
Al ₂ O ₃ . % .	6.31	6.03	7.64	7.22	12.86	6.71	6.38	3.41	2.99
Fe ₂ O ₃ . % .	0.68	0.03	1.24	0.03	3.72	0.78	0.03	0.48	0.02
FeO. % .	N.d.	0.03	N.d.	0.03	N.d.	N.d.	0.03	N.d.	0.02
TiO ₂ . % .	0.14	N.d.	0.43	N.d.	0.58	0.43	N.d.	0.18	N.d.
CaO. % .	0.12	0.03	0.09	0.03	0.41	0.13	0.03	0.08	0.01
MgO. % .	0.18	0.03	0.28	0.03	0.78	0.24	0.03	0.21	0.01
K ₂ O. % .	1.94	1.80	1.74	1.95	1.78	1.94	2.40	0.56	0.42
Na ₂ O. % .	0.24	0.32	0.41	0.35	0.81	0.68	0.40	0.18	0.08
H ₂ O. % .	1.18	0.92	1.48	1.21	3.95	1.20	0.81	0.81	0.84
Total. % .	99.90	99.98	100.06	99.97	99.92	99.88	100.01	99.96	100.04

N.d. = not determined.

PART 2.—THE LOWER CARBONIFEROUS SANDSTONES OF ROTHBURY FOREST AND ALNWICK MOOR, NORTHUMBERLAND.¹

(Figs. 39 to 46 — Plates V. and VI.)

SUMMARY.

These sandstones occur within easy reach of the Tyneside foundries. Geologically, they can be referred to two groups, *viz.*, the Fell Sandstone Group and the Scremerston Coal Group.

The sandstones of the former group are so friable that in many cases they can be crushed between the finger and thumb; the resultant sand contains 95% or more of quartz. By simple washing, the quartz content can be increased to more than 98%. Consequently the Fell Sandstones are of particular interest as a source of high-silica sand.

The sandstones of the Scremerston Coal Group in this area are, in general, too fine-grained and compact to be of use for steel moulding, though one (R2), from near Rothbury, may be of service.

I.—INTRODUCTION.

The localities from which these Lower Carboniferous sandstones were obtained are indicated on the sketch map, Fig. 35. Most of the massive sandstones of Rothbury Forest and Alnwick Moor are referred by the Geological Survey to the Fell Sandstone Group of the Lower Carboniferous; those from localities R2 and R7 are referred to the Scremerston Coal Group.

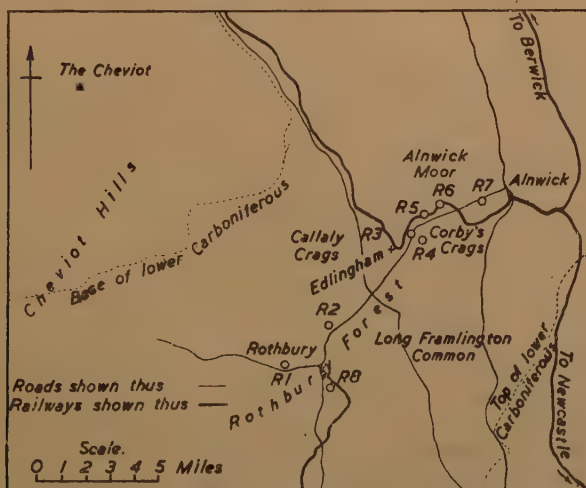


FIG. 35.—Sketch Map indicating the Localities Examined.

The Fell Sandstones of this district are possible sources of high-silica sand for steel-moulding purposes; according to local informa-

¹ Received November 2, 1942.

tion, sandstone near locality R8 (see Table XI.) was used for this purpose during the Great War. The sandstone from locality R2 is of interest as a source of medium-grained natural moulding sand. The sandstone from locality R7 is too fine-grained and compact to be of much interest.

TABLE XI.—*Index to Localities.*

Ref. No.	Stratigraphical Group.	Locality.
R1	Fell Sandstone.	Disused quarry overlooking the by-road at Pondicherry, $\frac{1}{2}$ mile west of Rothbury Church.
R2	Scremerston Coal.	Disused quarry adjoining the Rothbury-Alnwick road, $1\frac{1}{4}$ miles north-east of Rothbury Church.
R3	Fell Sandstone.	Crag just below the Rothbury-Alnwick road at Corbys Crag, $4\frac{1}{2}$ miles west-south-west of Alnwick.
R4	Fell Sandstone.	Crag just above the Rothbury-Alnwick road at Corbys Crag, 4 miles west-south-west of Alnwick.
R5	Fell Sandstone.	Railway cutting west of Banktop, $3\frac{1}{2}$ –4 miles west-south-west of Alnwick.
R6	Fell Sandstone.	Railway cutting north of Townlaw Cairn, $2\frac{1}{2}$ miles west-south-west of Alnwick.
R7	Scremerston Coal.	Disused quarry adjoining the Rothbury-Alnwick road, 1 mile from Alnwick.
R8	Fell Sandstone.	Crag overlooking railway, $1\frac{1}{4}$ mile south-east of Rothbury Church.

The Fell Sandstones are so friable that in many cases they can be crushed between the finger and thumb. They are composed almost entirely of quartz; felspar usually forms less than 1% of the rock, while kaolin and secondary micas usually form less than 5%. After simple washing, the crushed sandstone has a high silica content, *e.g.*, 98% for locality R8.

As a consequence of their high quartz content, the Fell Sandstones form high crags, *e.g.*, Simonside Crag near Rothbury, and wild fells. Quarrying will affect only land of low agricultural value.

Transport facilities are good. Three of the localities adjoin branch-line railways, two more are within half a mile and the remainder within a mile of these railways.

Apparently no work on the use of these sandstones for moulding purposes has been published. The geology of the sandstones has been described by the Geological Survey.¹ Details are also given in an Appendix to this Part.

¹ "The Geology of the Alnwick District," pp. 18–35. *Memoirs of the Geological Survey of Great Britain*, 1932.

"The Geology of the Country around Rothbury, Ashington and Amble," pp. 13–21. *Memoirs of the Geological Survey of Great Britain*, 1935.

II.—STRATIGRAPHY.

The Geological Survey ¹ distinguishes the following sequence in the Lower Carboniferous sediments on the south-east flank of the Cheviot Hills :

	Limestone Group.
Bernician.	Scremerston Coal Group.
Tuedian.	Fell Sandstone Group.
	Cementstone Group.

Almost the whole of the Fell Sandstone Group is composed of sandstone. In the other groups, sandstone beds, lithologically indistinguishable from those of the Fell Sandstone Group, are interspersed among beds of shale and argillaceous limestone (cementstone). For this reason, most of the localities examined are on the outcrop of the Fell Sandstone Group. The samples from *R2* and *R7* (Scremerston Coal Group) were selected because they differed lithologically from most of the Fell Sandstones.

The outcrop of the Fell Sandstone is marked by the prominent escarpments and wild moorland of Rothbury Forest and Alnwick Moor. False bedding is so prevalent in this group that any estimation of thickness must be merely approximate. According to the Survey, the thickness is probably 800 ft. near Alnwick, while around Rothbury it probably exceeds 1000 ft.

III.—PETROLOGY.

Most of the Fell Sandstones of Rothbury Forest and Alnwick Moor are so friable that they separate completely into their constituent grains after a short period of light milling. Some of the sandstones crumble readily between the finger and thumb. In fact, on this flank of the Cheviot, they are "sand rocks" rather than sandstones; this lithology is in marked contrast with that of the Fell Sandstone farther north. The sandstones are readily weathered, and considerable spreads of the sandy wash lie at the foot of many of the crags, *e.g.*, Callaly Crags and Corby's Crags (*see* Fig. 35).

The Fell Sandstones are composed almost entirely of quartz; the only other minerals present are felspar, which rarely forms more than 1% of the rock, and a few per cent. of kaolin and micaceous minerals of the sericite-hydrobiotite group. The kaolin and micaceous minerals can scarcely be regarded as a bond in most of the rocks, for they merely fill a few of the pores between the sand grains. Patches of hematite- and limonite-bonded sandstones occur in the middle crags at Edlingham. The sand grains, par-

¹ "The Geology of the Alnwick District," *loc. cit.*, p. 2.

ticularly in the more friable sandstones, sparkle in the sunlight, owing to the development of crystal facets by secondary silicification.

The colour of the sandstones varies according to the extent and character of the iron-staining. The leached sandstones are usually greyish-white; as the proportion of limonite increases, the colour ranges through fawn to brown. Cross-sections of the beds exposed in quarry faces usually show the pattern of false-bedding marked out in shades of brown by the iron-staining. At one or two localities, the sandstone is pink, owing to hematite-staining.

Though the sandstones are extensively false-bedded, the grain size does not vary rapidly. For instance, at Pondicherry (R1), near Rothbury, the sandstone is even-grained over a face 30–40 ft. high and for a distance of 80 yards laterally. The pattern of the false-bedding is shown only by iron-staining and wind-fretting of the face. In the railway cuttings on Alnwick Moor (R5, R6) the grain size varies slightly from bed to bed, the beds being 10 ft. or more in thickness. Each bed is even-grained, and approximately 80% of the sand grains are of medium grade, *i.e.*, 0.25–0.50 mm. in dia. Conglomerate bands are uncommon, and rarely exceed an inch or two in thickness.

The sandstone at locality R7 near Alnwick is particularly fine-grained and contains scattered flakes of muscovite.

The sandstone at locality R2, north of Rothbury, adjoins a Tertiary dolerite (tholeiite) dyke. The sandstone is so ferruginous that many of the sand grains are separated by films of limonite and siderite.

Mineral Constituents.

Quartz.—The typical quartz grains at the Fell Sandstone localities show little or no sign of permanent strain and contain scattered inclusions. They were probably derived from acid igneous rocks such as granite. Typical examples are shown in Fig. 39.

Grains containing linearly arranged inclusions and showing marked strain shadows, and grains of quartzite are present in noteworthy proportion in the sandstone from locality R2 (Sermerston Coal Group) and in some of the beds at locality R8 (Fell Sandstone Group). Strain shadows and linearly arranged inclusions in quartz grains from locality R8 are shown in Fig. 45.

The shape of nearly all the quartz grains has changed considerably since these sandstones first accumulated. The original grains were subangular or even rounded, but corrosion and secondary silicification have given the grains a more angular shape. The sketches in Fig. 36 illustrate the shapes of the grains as originally deposited and their present shapes.

Corroded grains with corrugated outlines are conspicuous in Fig. 41. A good example of the development of crystal facets by the addition of secondary silica is to be seen in Fig. 40. The original rounded outline of the quartz grain is indicated by an

arrow; outside this original outline is a layer of secondary silica which has been deposited in optical continuity with the original grain and which shows the traces of four crystal faces.

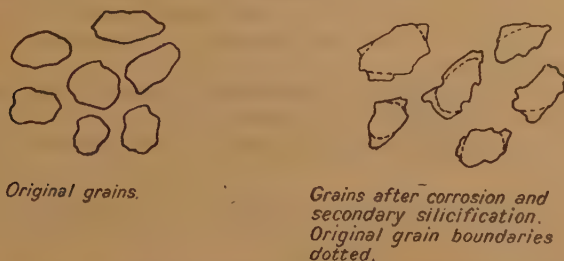


FIG. 36.—The Secondary Silicification of Quartz Grains. $\times 20$.

Felspar.—Microcline is the only felspar observed in the rocks examined. A grain with lamellar twinning can be distinguished on the left of Fig. 44. The microcline is slightly decomposed along the cleavages; consequently, it readily breaks down during milling into cleavage parallelepipeds. If the milled sandstone is washed, much of the felspar is removed, and the washed sand contains a negligible amount of felspar.

Muscovite.—With the exception of locality *R7*, muscovite mica is a very scarce constituent of the sandstones. At locality *R7* muscovite flakes are scattered through the rock and do not give it a flaggy character; a typical muscovite flake is indicated in Fig. 43.

Kaolin.—White clayey matter occurs interstitially in some of the sandstones. Under the microscope this is seen to have the vermicular platy habit characteristic of kaolin. When a sample of this material was examined by X-ray methods, it yielded a pattern of lines identical with those of Cornish china clay (kaolin). A kaolin pocket can be distinguished in Fig. 41.

Secondary Micas.—Some of the interstitial matter is micaceous in habit and is composed of secondary micas allied to the sericite-hydrobiotite group. In thin section the secondary micas appear as aggregates of yellow-polarising wisps; their polarisation colours are not so bright as those of muscovite. One such aggregate is indicated in Fig. 43.

Calcite and Siderite.—The sandstone at locality *R2* is closely cemented with calcite and siderite, associated with some limonite. The absence of rhomb-shaped crystals with curved faces suggests that dolomite is not present. This calcite-siderite bond forms most of the interstitial matter between the quartz grains in Fig. 46.

Heavy Minerals.

The proportion of non-opaque heavy minerals is small, usually about 0.10%, though it is as high as 0.15% in one or two samples.

The heavy minerals present are as follows ; their relative proportions are given in Table XII. :

Zircon is present in all the samples as rounded, colourless grains; the majority of the grains are elongated and some have pyramidal terminations. A few of the grains are zoned.

Rutile occurs either as reddish-brown or yellow angular-to-subangular grains.

Tourmaline is present as euhedral or rounded grains which are strongly pleochroic in shades of brownish-green.

Muscovite appears in the heavy-mineral residue as ragged flakes.

TABLE XII.—*Distribution of Heavy Minerals at the Eight Localities.*

Locality : Percentage of heavy minerals :*	R1. 0-08.	R2. 0-60.	R3. 0-20.	R4. 0-25.	R5. 0-08.	R6. 0-08.	R7. 0-10.	R8. 0-12.
Zircon . .	a	f	a	f	f	a	a	a
Rutile . .	r	r	r	f	r	f	r	f
Tourmaline .	f	r	f	f	f	f	f	f
Muscovite	r	f	...
Pyroxene	r	r	f	...	r
Siderite	f
Magnetite and limonite .	f	f	a	a	a	a	a	a
Ilmenite and leucoxene .	f	a	a	a	a	a	a	a

* These percentages include both opaque and non-opaque minerals.

a = abundant; f = frequent; r = rare.

Pyroxene is present at several of the Fell Sandstone localities and has probably been derived from the nearby Old Red Sandstone lavas of the Cheviot Hills. Most of the pyroxene is pale-green augite, though some appears to be hypersthene.

Siderite forms aggregates of brown grains having very high birefringence and is restricted to locality R2.

Magnetite and Limonite are both present in all the samples as well-rounded grains. The magnetite grains are coated with limonite and the two minerals were separated magnetically.

Ilmenite and Leucoxene are present; the ilmenite is more or less altered to leucoxene and may be distinguished magnetically from the magnetite.

Microstructure.

The microstructure of the Fell Sandstone at the localities examined does not vary greatly. The shape of the quartz grains has been changed by corrosion and the deposition of secondary silica, so that the grains fit more closely together than when the sandstone first accumulated. As a result, some of the sandstones are so compact that they are almost quartzites. The majority of the sandstones are, however, best described as even-grained sand rocks,

a term which emphasises their friable nature. The kaolin and secondary micaceous matter fill a few pores, but cannot be regarded as bonds.

The effects of this alteration of grain shape on the microstructure by the corrosion and deposition of silica are illustrated in Fig. 45. On the left of the field the pores between the grains have almost disappeared and the rock has taken on the character of a quartzite. The grains are not interlocked, and little pressure is needed to separate them; they are fitted together in much the same way as a brick wall built without mortar. In Figs. 40 and 42 this development of this compact microstructure is only rudimentary; in Figs. 39 and 41 it is more extensively developed, while its best development is seen in Fig. 43 (Scremerston Coal Group).

The closing of the pores increases the angularity of the grains and increases the strength of the rock appreciably. When the more compact types of sandstone are milled lightly they break down into angular grains, whereas the more open type of sandstone breaks down into subangular grains on milling. Under comparable conditions a green-sand mixture prepared from angular-grain sand has a higher green strength than one prepared from subangular grains. Consequently the ideal microstructure for moulding purposes is that in which the grains have become angular by the corrosion and the deposition of silica without closing the pores to such an extent that the rock cannot be crushed easily. The microstructures of the Fell Sandstones from all the localities examined are all suitable in this respect. The sandstone from the Scremerston Coal Group *R7* is too compact, and also too fine-grained, to be suitable for moulding purposes.

The sandstone from the Scremerston Coal Group *R2* has a microstructure different from that of the Fell Sandstones already described. Most of the quartz grains are separated by a bond of calcite, siderite and limonite, as shown in Fig. 46. Microstructures, such as that shown in Fig. 37, suggest that the deposition of the bond between some of the quartz grains was closely associated with the corrosion of the quartz grain. When the sandstone is crushed a film of this bond is left tightly attached to the corrugated surfaces of these corroded grains.

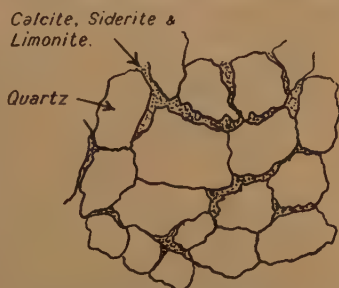


FIG. 37.—Microstructure of the Sandstone from Locality *R2*.
× 20.

IV.—CHEMICAL COMPOSITION.

The analyses of three of the coarser washed grits are given in Table XIII. Even with the simple washing employed, the sands

TABLE XIII.—*Analyses of Three Coarser Washed Grits.*

		R5.	R6.	R8.
SiO ₂ .	%	96.71	98.07	97.94
TiO ₂ .	%	0.06	0.08	0.17
Al ₂ O ₃ .	%	1.69	0.91	1.05
Fe ₂ O ₃ .	%	0.60	0.31	0.13
CaO.	%	0.00	0.00	0.00
MgO.	%	0.33	0.04	0.02
K ₂ O.	%	0.06	0.04	0.24
Loss on ignition.	%	0.55	0.55	0.45
Total.	%	100.00	100.00	100.00

have a high silica content and low alkali content. The alumina is present in the kaolin and secondary micas, which might have been removed by a more thorough washing. The iron in R5 is present partly as limonite; in R6 and R8 it is present mainly in the secondary micas, that is, the secondary micas tend to be chloritic.

V.—THE MOULDING CHARACTERISTICS OF THE CRUSHED SANDSTONES.

The Fell Sandstones contain such a small proportion of minerals other than quartz that their moulding characteristics are controlled almost entirely by the shape and size of the quartz grains.

Mechanical Grading.

As will be seen from Figs. 39 to 43, the sandstones are remarkably even-grained, the only exceptions being some of the beds at locality R8.

The sieve analyses of the crushed sandstones are given in Table XIV.; the cumulative gradings are recorded in Table XV., and

TABLE XIV.—*Mechanical Analyses of the Crushed Sandstones before Washing.*

B.S.I. Sieve No.	R1.	R2.	R3.	R4.	R5.	R6.	R7.	R8.
On 5. % .	0.0	0.0	0.1	0.0	0.0	0.5	0.5	0.0
" 10. % .	0.0	0.1	0.1	0.7	0.0	0.7	0.9	0.1
" 16. % .	0.2	6.5	0.1	4.6	1.6	2.1	4.1	4.4
" 22. % .	1.2	6.9	0.4	3.2	4.9	5.1	2.2	5.2
" 30. % .	2.9	23.1	6.1	4.8	13.0	13.4	2.6	11.3
" 44. % .	6.3	36.7	22.0	10.8	29.3	23.9	4.2	30.0
" 60. % .	14.0	7.2	35.5	19.3	21.8	20.2	7.2	24.6
" 72. % .	23.9	2.8	17.3	19.9	...	13.1	7.2	10.3
" 100. % .	33.3	4.2	9.6	23.4	19.6	11.8	28.6	4.6
" 150. % .	11.3	5.2	4.9	8.6	4.7	5.2	35.1	4.6
Thro' 150. % .	5.9	7.1	3.8	4.5	5.0	3.9	7.3	4.7
Total. % .	99.9	99.8	99.9	99.8	99.9	99.9	99.9	99.8

TABLE XV.—*Cumulative Grading of the Crushed Sandstones before Washing.*

B.S.I. Sieve No.				R1.	R2.	R3.	R4.	R5.	R6.	R7.	R8.
On	5.	%	.	0.0	0.0	0.1	0.0	0.0	0.5	0.5	0.0
"	10.	%	.	0.0	0.1	0.2	0.7	0.0	1.2	1.4	0.1
"	16.	%	.	0.2	6.6	0.3	5.3	1.6	3.3	5.5	4.5
"	22.	%	.	1.4	13.5	0.7	8.5	6.5	8.4	7.7	9.7
"	30.	%	.	4.3	36.6	6.8	13.3	19.5	21.8	10.3	21.0
"	44.	%	.	10.6	73.3	28.8	24.1	48.8	45.7	14.5	51.0
"	60.	%	.	25.5	80.5	64.3	43.4	...	69.9	21.7	75.6
"	72.	%	.	49.4	83.3	81.6	63.3	70.6	79.0	28.9	85.9
"	100.	%	.	82.7	87.5	91.2	86.7	90.2	90.8	57.0	90.5
"	150.	%	.	94.0	92.7	96.1	95.3	94.9	96.0	92.6	95.1

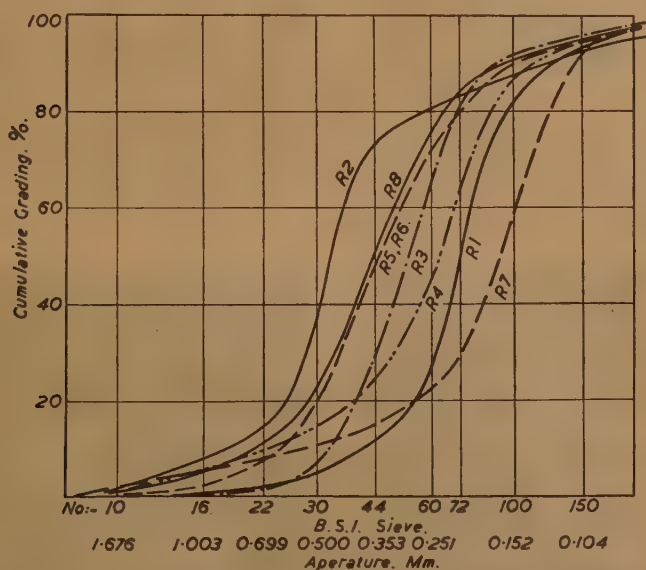


FIG. 38.—Cumulative Grading Curves for Crushed Sandstones.

shown graphically in Fig. 38. The even grading is indicated by the steep gradients of the central portions of the curves.

The sharp bend towards the top of the curve for the crushed sandstone from locality R2 is due to the high proportion of finely divided bond; the grading of the quartz grains is indicated by the portion of the curve below the 70% ordinate.

The curves for the crushed sandstones from localities R1 and R3 are rather steeper than those for the other Fell Sandstones, indicating that the former are particularly even-grained. Comparison between the crushed sandstones from localities R3 and R1

should show the effect of a decrease in the average grain size on the strength and permeability. The crushed sandstones from localities *R5*, *R6* and *R8* have almost identical gradings and may be expected to have the same strength and permeability. These three sandstones are coarser than that from locality *R4* and much coarser than that from locality *R7*; the curves for these five sandstones are parallel, and consequently they should show the effect of average grain size on the other moulding properties.

TABLE XVI.—*Mechanical Analyses of the Crushed Sandstones after Washing.*

B.S.I. Sieve No.	<i>R1.</i>	<i>R2.</i>	<i>R3.</i>	<i>R4.</i>	<i>R5.</i>	<i>R6.</i>	<i>R7.</i>	<i>R8.</i>
On 5. % .	0.0	0.0	0.0	0.0	0.0	0.0	...	0.0
" 10. % .	0.0	0.0	0.10	0.5	0.1	0.7	...	0.4
" 16. % .	0.1	3.8	2.8	3.6	4.3	4.9	...	3.1
" 22. % .	0.3	5.1	2.2	2.9	4.0	5.4	...	2.8
" 30. % .	2.1	21.8	4.6	5.1	11.6	16.6	...	10.6
" 44. % .	7.8	48.5	15.2	11.7	27.1	28.2	...	29.8
" 60. % .	27.0	11.2	45.9	30.4	32.0	27.3	...	38.4
" 72. % .	20.5	...	14.2	28.0	8.4	7.1	...	7.5
" 100. % .	32.6	6.3	8.2	10.5	8.6	7.7	...	5.8
" 150. % .	7.9	2.4	4.5	6.4	2.8	1.6	...	1.5
Thro' 150. % .	1.7	0.7	2.1	0.7	0.8	0.4	...	0.2
Total % . .	100.0	99.8	99.8	99.8	99.7	99.9	...	100.1
Yield after washing. %	93	86	95	88	88	87	50	84

The crushed sandstones were washed in water containing a trace of ammonia, in order to remove the fines. The mechanical analyses of the washed sandstones are given in Table XVI. and the cumulative gradings in Table XVII.

TABLE XVII.—*Cumulative Grading of the Crushed Sandstones after Washing.*

B.S.I. Sieve No.	<i>R1.</i>	<i>R2.</i>	<i>R3.</i>	<i>R4.</i>	<i>R5.</i>	<i>R6.</i>	<i>R7.</i>	<i>R8.</i>
On 5. % .	0.0	0.0	0.0	0.0	0.0	0.0	Too fine to be washed satisfactorily.	0.0
" 10. % .	0.0	0.0	0.10	0.5	0.1	0.7		0.4
" 16. % .	0.1	3.8	2.90	4.1	4.4	5.6		3.5
" 22. % .	0.4	8.9	5.1	7.0	8.4	11.0		6.3
" 30. % .	2.5	30.7	9.7	12.1	20.0	27.6		16.9
" 44. % .	10.3	79.2	24.9	23.8	47.1	55.8		46.7
" 60. % .	37.3	90.4	70.8	54.2	79.1	83.1		85.1
" 72. % .	57.8	87.5	90.2		92.6
" 100. % .	90.4	96.7	93.2	92.7	96.1	97.9		98.4
" 150. % .	98.3	99.1	97.7	99.1	98.9	99.5		99.9

Comparisons between Tables XVI. and XVIII., giving the gradings of some high-silica sands, show that the washed sand from locality *R1* is rather finer than Chelford sand. The washed sand-

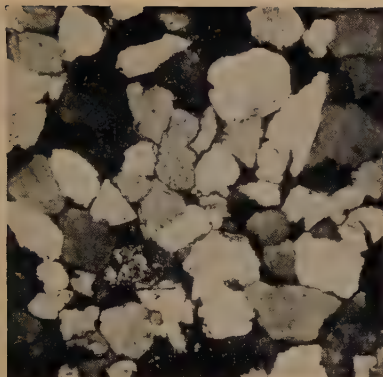


FIG. 39.—Fell Sandstone, R6. Even-grained, friable sandstone of medium grade composed of unstrained quartz grains containing scattered inclusions. Most grains show signs of corrosion. $\times 20$, crossed nicols.

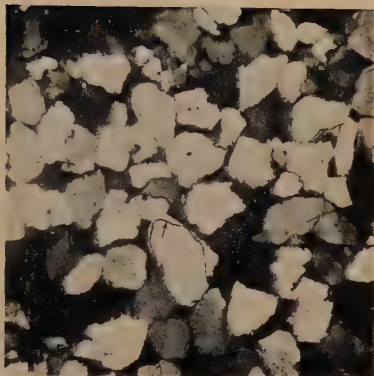


FIG. 40.—Fell Sandstone, R3. Even-grained, friable sandstone of medium grade. Many grains have coating of secondary silica. Original outline of one such grain indicated by an arrow. $\times 30$, crossed nicols.

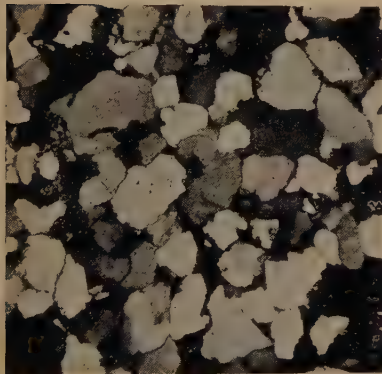


FIG. 41.—Fell Sandstone, R3. Even-grained, friable sandstone of medium grade; quartz grains have corrugated outlines produced by corrosion. Kaolin pocket (K). $\times 30$, crossed nicols.

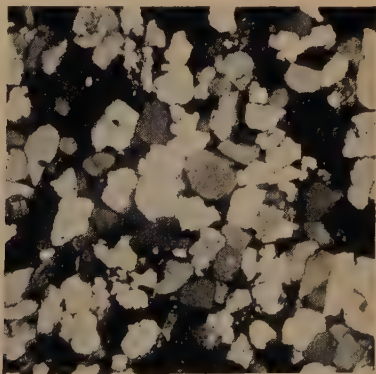


FIG. 42.—Fell Sandstone, R1. Even-grained, friable sandstone of fine grade composed of unstrained quartz grains containing scattered inclusions. $\times 30$, crossed nicols.

(Micrographs reduced to four-fifths linear in reproduction.)

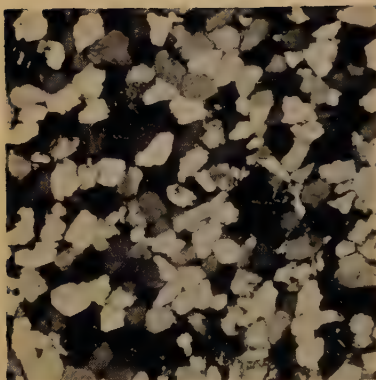


FIG. 43. —Sandstone (Scremerston Coal Group), R7. Even-grained compact sandstone of fine grade; grain shape altered by secondary silicification until the grains fit closely together. $\times 30$, crossed nicols.

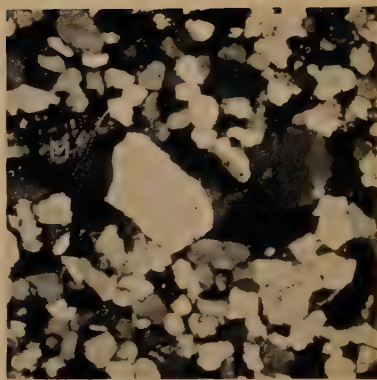


FIG. 44. —Fell Sandstone, R8. Friable sandstone composed of alternate thin coarse-grained and thick fine-grained bands. Microcline feldspar (M). $\times 30$, crossed nicols.

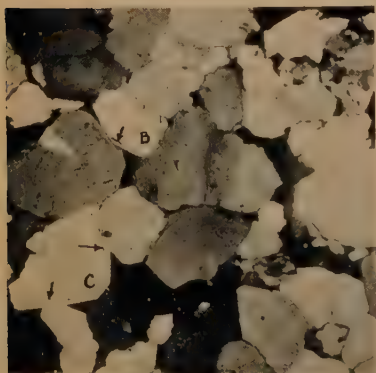


FIG. 45. —Fell Sandstone, R8. Alteration of shape by corrosion (A) and by addition of secondary silica (B). Crystal facets formed on some grains by this secondary silica (C). Original grain boundaries indicated by arrows. $\times 50$, crossed nicols.

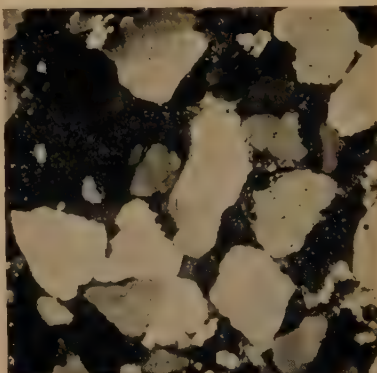


FIG. 46. —Sandstone (Scremerston Coal Group), R2. Coarse-grained sandstone composed of corroded quartz grains bonded together by calcite, siderite and limonite. Quartzite grain (Q). $\times 30$, crossed nicols.

(Micrographs reduced to four-fifths linear in reproduction.)

TABLE XVIII.—*Mechanical Analyses of some High-Silica Sands.**

B.S.I. Sieve No.		Leighton Buzzard No. 52.	Chelford.	Aylesbury No. 60.
On 16.	% . .	0.2	0.1	0.2
„ 22.	% . .	1.0	0.4	0.3
„ 30.	% . .	8.8	3.2	0.6
„ 44.	% . .	60.5	17.5	2.7
„ 60.	% . .	27.3	40.0	13.4
„ 100.	% . .	2.0	34.2	65.8
„ 150.	% . .	0.2	3.9	14.4
Thro' 150.	% . .	0.1	0.7	2.6

* First Report of the Moulding Materials Sub-Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 23*, pp. 143–144.

stones from localities *R3* to *R6* and *R8* have gradings which lie between those for Leighton Buzzard No. 52 and Chelford sands.

Even after prolonged washing, much of the bond of *R2* still adheres to the grains. The grading is not quite so coarse as that of Leighton Buzzard No. 52 sand.

Green Strength.

With the exception of *R2*, the maximum green strength of the natural crushed sandstones is very low, owing to the absence of bonding minerals in the natural rocks.

The crushed sandstone from *R2* has a comparatively high green strength and good permeability, owing to its natural bond. Its properties are summarised below :

Moulding Properties of R2.

	3 Rams.	10 Rams.
Maximum green strength	7 lb. per sq. in.	11 lb. per sq. in.
Moisture content	4%	4%
Permeability number	95	62
Dry strength	18 lb. per sq. in.	25 lb. per sq. in.

Tests were made on the other sandstones after the addition of 5% of ball clay; they were repeated with the washed sands in order to determine the effect of removing the fines. The results are recorded in Table XIX. The removal of the fines from *R1* and *R4* reduces the green strength and greatly increases the permeability, that is, the fines in both cases are composed of finely divided quartz rather than clay minerals. Comparison of the washed and unwashed sands from *R3* and *R5* suggests that a large proportion of the fines at both localities is composed of clay minerals which are helping to bond the sand.

Some of the unwashed crushed sandstones, particularly *R1* and *R5*, with the addition of 5% of ball clay have green strengths and permeability numbers comparable with green-sand mixes used in steel foundries.

The green strengths and permeability numbers of the washed sands bonded with 5% of ball clay are in accord with their grading.

TABLE XIX.—*The Green Strength and Permeability of the Crushed Sandstones.*

5% of ball clay added.

	R1.	R3.	R4.	R5.	R8.
Maximum green strength, lb. per sq. in. :					
Rammed 3 times, unwashed.	5.7	3.7	3.3	6.6	3.1
" 3 times, washed .	4.6	1.8	3.0	2.4	...
" 10 times, unwashed .	8.5	6.2	5.7	9.9	4.9
" 10 times, washed .	6.1	3.0	4.5	3.5	...
Moisture content, % :					
Unwashed	4	4	4	4	4
Washed	3	3	3	3	3
Permeability number :					
Rammed 3 times, unwashed.	79	129	196	100	142
" 3 times, washed .	111	216	152	229	...
" 10 times, unwashed.	59	96	68	73	96
" 10 times, washed .	80	163	106	197	...

Dry Strength.

The dry strengths of the unwashed sands bonded with 5% of ball clay are as follows :

Locality	R1.	R3.	R4.	R5.	R8.
Dry strength. Lb. per sq. in. .	24	16	16	22	15

(Leighton Buzzard No. 52: 20 lb. per sq. in.)

They are of the same order as the strength of Leighton Buzzard No. 52 sand bonded with 5% of ball clay. The test-pieces were prepared from mixes containing 4% of moisture and were rammed three times. After drying at 200° C. for 2 hr. they were allowed to cool to room temperature and then crushed.

TABLE XX.—*Refractoriness.*

A.F.A. test-pieces bonded with 5% of Fulbond No. 1 and fired at 1550° C. for 2 hr.

Sand No.	Shrinkage. %.		Remarks.
	Length.	Diameter.	
R1	7.5	7.5	White. Grains well fritted.
R2	10.0	10.0	Brown. Test-piece glazed and distorted.
R3	2.5	2.5	White. Grains slightly fritted.
R4	2.5	2.5	White. Grains fritted.
R5	2.5	2.5	White. Grains fritted.
R6	2.5	2.5	White. Grains fritted.
R7	10.0	10.0	White. Grains well fritted.
R8	0.0	0.0	White, with slight mottling. Grains scarcely fritted.

Refractoriness.

The results of refractory tests on the crushed sandstones, bonded with 5% of Fulbond No. 1 and fired at 1550° C. for 2 hr., are recorded in Table XX.

VI.—CONCLUSIONS.

The Fell Sandstones from localities *R5*, *R6* and *R8* after crushing and washing yield sands composed of clean angular-to-subangular grains; 70% of these grains have diameters between 0.50 and 0.25 mm. The silica content of the sands after washing ranges from 97 to 98%.

The sandstones from localities *R1*, *R3* and *R4* are finer-grained than those mentioned above. After crushing and washing, about 80% of the sand from *R1* was composed of grains 0.35–0.15 mm. in dia.; 75% of that from *R3* and 70% of that from *R4* were composed of grains 0.35–0.20 mm. in dia. The washed grains were clean and angular-to-subangular in shape. No chemical analyses were made, but it is probable that their silica content is greater than 96%.

With the possible exception of *R2* and *R7*, the sands produced by crushing these sandstones appear to be sufficiently refractory for steel-foundry use. After washing they are comparable in character with high-silica sands of similar grading from other sources, such as Leighton Buzzard.

The sandstone from locality *R2* is of interest as a natural moulding sand of coarser grade than those of Bunter age. It is more even-grained and permeable than Tow Law sand,¹ though its dry strength is decidedly lower.

APPENDIX.—*Detailed Petrological Descriptions of the Rock Samples from Localities R1 to R8.*

(The species present in the heavy-mineral assemblages are described in Sub-Section III.)

R1, Fell Sandstone Group.

Situation.—Disused quarry overlooking the by-road at Pondicherry, $\frac{3}{4}$ mile west of Rothbury Church. The land adjoining the quarry is rough fell.

Transport Facilities.—The quarry is connected to Rothbury Station by a good road, the distance being $1\frac{1}{4}$ mile. The station is the terminus of a branch line from Morpeth.

Petrological Description.

The sandstone is well exposed at this locality. It is an even-grained sandstone of fine grade, of which the colour banding in shades of light brown suggests the pattern of false-bedding; the false-bedding is not shown by any variation in grain size. It has an open texture

¹ First Report of the Moulding Materials Sub-Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 23*, p. 197.

and is extremely friable. Many of the grains have developed crystal facets, owing to the deposition of secondary silica. The uniform grain size has already been emphasised in Sub-Section III. The proportion of minerals other than quartz is very small; these minerals include felspar, muscovite, kaolin, secondary micas and limonite. The quartz occurs as simple, unstrained grains, 0.35–0.15 mm. across; inclusions are not abundant and are not linearly arranged. The grains are either angular, owing to the development of crystal faces by the addition of secondary silica, or else have a corrugated form due to corrosion. Grains of quartzite are rare. The felspar forms less than 1% of the rock; most of the grains can be identified as microcline micropertthite and are slightly decomposed along the cleavage cracks. Muscovite flakes are rare; they are bent to accommodate the adjacent quartz grains. Kaolin is present in greater proportion than the felspar; it shows the characteristic fan-like and vermicular structures and has very low polarisation colours. The secondary micas are closely associated with the kaolin; they are almost colourless, which suggests that they are sericitic rather than chloritic. Limonite occurs as thin films between the quartz grains or on the original surface of grains which have been coated with secondary silica.

The heavy-mineral assemblage includes zircon, rutile and tourmaline and the usual opaque species.

The sandstone has a fairly open texture. Corrosion and the deposition of secondary silica have increased the angularity of the grains, but the quartzitic structure is but feebly developed (*see* Fig. 39); dovetail suturing of the quartz grains is extremely rare. The kaolin and secondary micas occur interstitially, and appear to be detrital rather than pseudomorphs after felspar grains which have decomposed since the sandstone first accumulated.

The sandstone breaks down readily into its constituent grains after a short period of light milling. Washing removes about 7% of the milled rock. The majority of the washed grains were subangular and clean; some were slightly coated with limonite. About 80% of the washed material has grain sizes in the range 0.35–0.15 mm., that is, the washed sand is rather coarser than Chelford sand.

R2, Seremerston Coal Group.

Situation.—Disused quarry adjoining the Rothbury–Alnwick road, 1½ mile north-east of Rothbury Church. The quarry cuts into rough moorland.

Transport Facilities.—The quarry is connected to Rothbury Station by a good road, the distance being about 2 miles. The station is the terminus of a branch line from Morpeth.

Petrological Description.

This quarry has been opened partly in a tholeiite dyke (the Acklington dyke) and partly in sandstone. The former was worked for road stone, while the latter was used for nearby walls and buildings.

The sandstone is even-grained and of coarse-to-medium grade. It is well bonded and far more compact than the Fell Sandstones examined. The bond gives the rock a brown colour. Some of the grains have facets due to the deposition of secondary silica. The rock is mainly of interest as a fairly coarse moulding sand.

The sandstone is composed essentially of quartz, siderite and calcite, together with a small proportion of felspar, kaolin, secondary

mica and limonite. The quartz occurs both as grains of quartzite and as single large grains. The former show suturing and strain shadows usually seen in quartzite the structure of which is due to regional metamorphism; they are the same size as the large single grains, that is, 0.70–0.35 mm. in dia. The latter contain linearly arranged inclusions, and show strain shadows. The siderite, calcite and limonite are closely associated; together they constitute 11–12% of the rock. The siderite merges into limonite towards the outer portions of these aggregates. The feldspar is partly decomposed and is a microcline microperthite; it forms less than 0.5% of the rock. The secondary micas and kaolin are interstitial and are similar to that from locality R1.

The heavy-mineral assemblage is composed mainly of siderite and limonite. The other species present are zircon, rutile and tourmaline.

The microstructure is unusual. Some of the quartz grains have become quartzite aggregates by corrosion and deposition of silica. Others are corroded and separated by a layer of limonite. Some are deeply corroded, and appear to be isolated in a matrix of siderite and calcite (*see* Fig. 46).

Owing to its compact texture, the sandstone is decidedly stronger than the others described in this Part. Jaw-crushing followed by milling or even milling alone is sufficient to separate the grains completely. Each grain is well coated with natural bond. Much of the natural bond adheres to the quartz grains even after thorough washing.

R3, R4, Fell Sandstone Group.

Situation.—Corby's Crags on the Rothbury–Alnwick road, $4\frac{1}{2}$ miles west-south-west of Alnwick. The middle crag, just below the road, is referred to as R3, and the upper crag, just above the road, is referred to as R4.

Transport Facilities.—Corby's Crags overlook the branch railway from Alnwick; R3 is about 300 yards and R4 about 600 yards from the railway.

Petrological Description.

The Fell Sandstone is well exposed at these two localities. It is a friable sandstone of medium grade. The grain size varies slightly. The development of crystal facets by the deposition of secondary silica is very marked, and on a sunny day the crag faces sparkle. The colour varies from the pale browns associated with traces of limonite to the dull red due to hematite and the greyish white of the leached rock. Except in one or two isolated patches, there is little interstitial matter, the limonite and hematite being present in just sufficient quantity to stain the rock.

At both localities the rock is composed almost entirely of quartz; the other minerals present include feldspar, kaolin, secondary micas, muscovite, limonite and hematite. The quartz occurs as simple unstrained grains containing scattered inclusions. The grain size ranges from 0.35 to 0.25 mm. at R3, and from 0.35 to 0.20 mm. at R4, that is, the rock at R3 is more even-grained than that at R4. Some of the quartz grains are so corroded that they have developed a lobate outline, without any interlocking of the grains. Many of the grains are more or less coated with secondary silica. The feldspar is microcline microperthite and is slightly decomposed along the cleavages; it constitutes less than 1% of the rock. The kaolin and secondary mica are present in greater proportion than the feldspar; they both occur as

platy aggregates, the former having low polarisation colours and the latter fairly high colours. There are a few scattered flakes of muscovite at locality R3. The limonite and hematite form the bond between some of the quartz grains.

The heavy-mineral assemblage includes zircon, rutile and tourmaline at both localities. In addition, pyroxene occurs at R4.

The sandstone has an open texture. Grain corrosion and the deposition of secondary silica have affected the shapes of most of the grains (see Figs. 40 and 41). Dovetail suturing of the quartz grains is extremely rare. The kaolin and secondary micas are interstitial and appear to be detrital.

The sandstone is crushed readily. After washing, the crushed sandstone is composed of subangular-to-angular grains, the majority of which are clean. A few of the grains are slightly coated with limonite. About 75% of the grains in R3 and about 70% in R4 have diameters between 0.35 and 0.20 mm.

R5, R6, Fell Sandstone Group.

Situation.—Railway cuttings on the Alnwick-Coldstream branch line of the London and North-Eastern Railway. Locality R5 is $3\frac{1}{2}$ –4 miles and locality R6 $2\frac{1}{2}$ miles west-south-west of Alnwick.

Transport Facilities.—The above-mentioned branch line joins the main line at Alnmouth, which is about 20 miles north of Newcastle.

Petrological Description.

These two railway cuttings provide two of the finest sections of the Fell Sandstone in this district. Except for a few conglomerate bands, which rarely exceed an inch or two in thickness, the Fell Sandstone here consists of thick beds of medium-grained sandstone. The grain size varies slightly from bed to bed—over 80% of the grains in the crushed rock are of medium grade. The sandstone is friable and is stained with limonite. One or two thin layers are bonded by limonite, but in most of the beds the only minerals present besides quartz are feldspar and its decomposition products.

Nearly all the quartz is present as simple unstrained grains containing scattered inclusions; there are a few grains of quartzite. The grain size ranges from 0.5 to 0.2 mm. Corrosion has given some of the quartz grains a lobate outline without any interlocking of the grains. Many of the grains are more or less coated with secondary silica, often with the formation of crystal facets. The feldspar is rather more abundant than at the other localities, but, even so, it constitutes less than 2.5% of the rock; it is microcline micropertite and is slightly decomposed along the cleavages. The decomposition products of the feldspar, i.e., kaolin and secondary micas, form platy aggregates, and are rather more abundant than the feldspar.

The heavy-mineral assemblage includes zircon, rutile, tourmaline and pyroxene, together with the usual opaque minerals magnetite, limonite, ilmenite and leucoxene.

Though grain corrosion and the deposition of secondary silica have altered the shape of most of the grains, these sandstones still have an open texture. Such strength as these rocks possess is not due to the interlocking of the grains but to their packing consequent on their alteration in shape; the kaolin and secondary micas are interstitial and do not occur in such proportion that they can be regarded as a bond (see Fig. 39).

The sandstone crushes easily, and the resulting sand, after washing, is composed of clean light-brown angular-to-subangular grains, some of which are slightly coated with limonite. About 70% of the grains at both localities have diameters between 0.50 and 0.25 mm.

R7, Scremerston Coal Group.

Situation.—Disused quarry adjoining the Rothbury-Alnwick road, one mile from Alnwick.

Transport Facilities.—The nearest railway is at Alnwick.

Petrological Description.

The rock exposed in the quarry face is fine-grained and compact; its colour varies from light brown near the joints to pink away from them.

This sandstone is of much finer grade than the others described in this Part; nearly all the grains are between 0.10 mm. and 0.20 mm. in dia. In the mechanical analysis (Table XIV.) the grains larger than 0.20 mm. (No. 72 sieve) are composite. The other minerals present besides quartz are feldspar and its decomposition products and muscovite, together with a trace of limonite and hematite. The quartz occurs as small angular grains containing scattered inclusions; quartzite grains are rare. The feldspar is microcline micropertthite and forms less than 1% of the rock. The kaolin and secondary micas occur as typical platy aggregates, and are of rather finer grain size than those in the other rocks. The muscovite occurs in ragged flakes.

The heavy-mineral assemblage includes zircon, rutile, tourmaline and the opaque minerals magnetite, limonite, ilmenite and leucoxene.

The microstructure is compact. Grain corrosion and secondary silicification have altered the grain shape until the microstructure approaches that of a quartzite. The muscovite flakes are scattered through the rock (see Fig. 43).

It is not possible to improve the proportion of sand by washing the crushed sandstone, as it is too fine-grained.

R8, Fell Sandstone Group.

Situation.—Crag overlooking the railway, 1½ mile south-east of Rothbury Church.

Transport Facilities.—The crag is about 100 yards from this railway, which connects Rothbury to Morpeth.

Petrological Description.

Most of the beds exposed in this crag are composed of even-grained sandstone and are of medium grade. One or two beds show false-bedding, and are formed of alternating layers of medium- and fine-grained sandstone. Faceting of the grains, due to the deposition of secondary silica, is well developed. The colour varies from light brown in the fresh rock to grey in the leached rock. Interstitial decomposed feldspathic matter is not abundant.

The other minerals present besides quartz are feldspar, kaolin, secondary micas and limonite. The quartz occurs as angular-to-subangular grains and as grains of a quartzite. Most of the grains are 0.50–0.25 mm. in dia., though some beds contain a proportion of grains between 0.25 and 0.15 mm. in dia. The inclusions are scattered in some of the grains and linearly arranged in others (see Fig. 45).

The feldspar forms less than 1% of the rock; it is a microcline microperthite, and is slightly decomposed along the cleavages. The kaolin and secondary micas are stained by limonite; they occur as typical platy aggregates.

The heavy-mineral assemblage includes zircon, rutile, tourmaline, ilmenite and leucoxene.

The sandstone has an open texture, though grain corrosion and the deposition of secondary silica have helped the grains to pack together, as will be seen in Fig. 45. Some of the beds have the microstructure shown in Fig. 44, due to false-bedding.

A bulk sample of the sandstone from the crag was crushed and washed. About 70% of the grains in this washed sand had diameters between 0.50 and 0.25 mm. The grains were angular-to-subangular in shape and most of them were clean; a few were slightly covered with limonite.

PART 3.—THE MOOR GRIT OF NORTH-EAST YORKSHIRE.¹

(Figs. 51 to 62 = Plates VII. and VIII.)

SUMMARY.

This grit occurs within easy reach of the Tees-side foundries. Two types of grit may be distinguished, viz., feldspathic and quartzitic.

Certain of the occurrences of the feldspathic type are sufficiently coarse to be suitable for use as steel-moulding sands; details of their moulding properties are given.

The texture of the quartzitic type varies from open to compact. The former variety can be crushed easily to yield a high-silica sand suitable for use in iron and steel foundries. The latter variety is of little interest for moulding-sand purposes, as it is difficult to crush, and the grading of the resultant sand is unsuitable.

I.—INTRODUCTION.

The greater part of the North Yorkshire Moors is underlain by Jurassic sandstones and shales of estuarine or deltaic origin. One of the most prominent of these sandstones is known as the Moor Grit. Its outcrop is partly obscured by glacial drift, but good exposures occur along the Esk Valley, on the Cleveland Hills near Osmotherly, and in the valleys which notch the escarpments along the southern edge of the Moors.

The Moor Grit varies from a fine-grained sandstone to a medium-grained grit and furnishes a good freestone at many localities. It is extremely false-bedded, and some of the lenses, particularly those close to the top of the Grit, are so compact and quartzose that they may well be described as quartzites rather than as sandstones. This quartzite is usually referred to locally as "white flint."

The normal Moor Grit is rather feldspathic and is being worked at one locality for moulding sands for use on Tees-side. The quartzitic

¹ Received November 2, 1942.

tic variety (white flint) is worked for silica-brick manufacture at several localities. Only the iron-free portion of the white flint is suitable for this purpose, and the remainder, which is slightly iron-stained, is thrown on the tip. This discarded material is a potential source of high-silica sand for steel-moulding purposes.

Transport facilities are fairly good. The localities examined along the Esk Valley are within a mile of the railway which connects to Middlesbrough, less than 20 miles away. Localities closer to the railway could probably be found, though trial holes would have to be made through the thin cover of the peat and boulder clay which obscure much of the outcrop. According to the Geological Survey, the Moor Grit is exposed in the railway cutting by Larpool Hall, one mile south of Whitby; this locality was not visited, owing to the difficulty of access.

The localities on the Cleveland Hills are several miles from the nearest railway station, which is about 10 miles from Stockton-on-Tees; those along the southern edge of the moors are 2-3 miles from the Pickering-Hemsley railway line.

There is no reference in the available literature to the use of the Moor Grit for moulding purposes, though the Geological Survey¹

TABLE XXI.—*Index to Samples.*

Ref. No.	Locality.
Y1	Roadside exposure; Hazel Heads, 6 miles east-south-east of Osmotherly.
Y2	Disused quarry; Solomon's Temple, 1½ miles east of Osmotherly.
Y3	Roadside exposure; Vear Moor, 1½ miles north-east of Osmotherly.
Y4	Disused Quarry; Blackshire, 1½ miles north north-east of Osmotherly.
Y5	Moorland exposure; Castleton/White-Cross Road, ½ mile north-north-west of Castleton Station.
Y7(a)	New Top Quarry; General Refractories, Ltd., Castleton Quarries.
Y7(b)	Lower (Moulding Sand) Quarry; General Refractories, Ltd., Castleton Quarries.
Y8(a) & (b)	Doubting Castle Quarry; ¾ mile north of Danby Station.
Y9	Clitherbeck Quarry; ¾ mile north-north-east of Danby Station.
Y10	Roadside exposure; Spindle Thorn, 2 miles north-north-east of Hutton-le-Hole.
Y11	Roadside exposure; above Lowna, 1 mile north-north-east of Gillamoor.
Y12	Roadside exposure; Hazel Green, 2½ miles north of Helmsley.
Y13	Disused quarry; Old Fold, 2 miles north of Helmsley.
Y14	Moorland exposure; Old Fold, 2 miles north of Helmsley.

¹ "The Jurassic Rocks of Britain." Vol. I., "Yorkshire," p. 147 *et seq.* *Memoirs of the Geological Survey of Great Britain*, 1892.

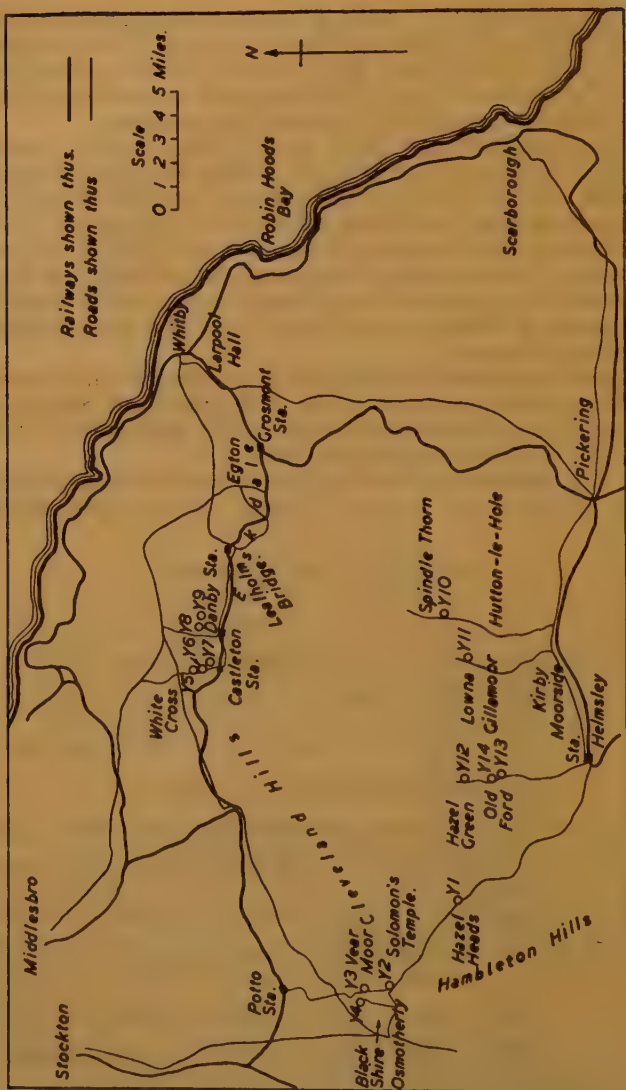


FIG. 47.—Sketch Map of North-East Yorkshire.

have described its geology in detail. R. H. Rastall¹ has given a general account of some of the Jurassic sandstones (including Moor

¹. "The Petrography of Some Jurassic Sandstones in Eskdale," *Proceedings of the Yorkshire Geological Society*, 1931-34, vol. 22, p. 93 et seq.

Grit) in Eskdale. F. Smithson¹ has described the heavy-mineral assemblages of the Jurassic rocks in detail.

The localities from which the samples were obtained are listed in Table XXI. and indicated on the sketch map Fig. 47. They are described in an Appendix to this Part.

II.—PETROLOGY.

It has already been indicated that two types of Moor Grit may be distinguished. The normal variety is felspathic, that is, besides quartz it contains a noteworthy proportion of felspar and its decomposition products. Limonite and muscovite are also present at some localities. Its colour ranges from pale yellow to dark brown. The texture is fairly compact, for the felspathic material occupies the pores between many of the quartz grains.

The quartzitic or white flint type is composed of little else but quartz; the only other noteworthy minerals are kaolin and secondary mica. It varies in colour from white to brown. At some localities the texture is open and the quartz grains sparkle in the sunlight, owing to the development of crystal facets by secondary silicification. At other localities the texture is compact and the rock breaks into flakes on crushing, that is, the fracture passes through, not around, the constituent grains.

Constituent Minerals.

Quartz.—The greater part of the quartz is present as single unstrained grains containing scattered bubble inclusions; a small proportion of the quartz is strained (indicated by undulose extinction). Grains of quartzite are rare; such as do occur are probably derived from schists. On these grounds it may be suggested that the quartz was derived from acid igneous rocks such as granite.

In almost every case, the shape of the quartz grains has changed since deposition. Many of the quartz grains are deeply pitted by corrosion, thereby forming an excellent surface for the attachment of an artificial bond, as shown in Fig. 48 (a). Such pitting is shown by many of the grains in Fig. 53. In some cases secondary silica has been deposited in optical continuity with the original grain, and, where growth has not been restricted by adjacent grains, the grain now has a polygonal outline due to the development of crystal facets, as shown in Fig. 48 (b). One such grain is shown in the centre of Fig. 53.

Though the majority of the grains are free from weaknesses, due to permanent strain and to linearly arranged inclusions, which would assist fracture during milling, the pitting of the corroded grains leads to the concentration of internal stress around the pits when the grain is loaded and so assists the development of fractures.

¹ "The Petrography of the Jurassic Sediments in Yorkshire," *Proceedings of the Yorkshire Geological Society*, 1931-34, vol. 22, p. 188 *et seq.*

Consequently, the crushed and milled rock composed of corroded grains has a finer grading than might be expected from the grain size of the original rock.

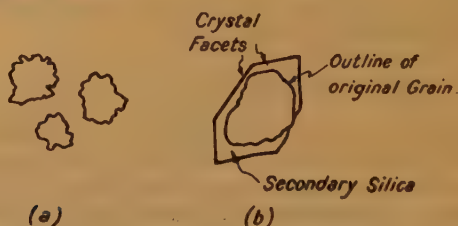


FIG. 48.—(a) Corrosion and (b) Secondary Silicification of Quartz Grains.

Microcline.—This feldspar is present as rounded grains which, in most cases, show no sign of decomposition. Cross-hatching and cleavage cracks are well-developed. In no case does the proportion of feldspar exceed 10%; in general it forms about 5% of the feldspathic type of Moor Grit. Typical grains can be seen in Fig. 51.

Muscovite.—This occurs in a few of the samples and is never abundant. The flakes may be scattered irregularly through the rock or else restricted to the bedding planes. At one or two localities muscovite is associated with a more or less bleached, ferromagnesian mica resembling biotite.

Secondary Micas.—Those micas which contain more water than muscovite are abundant in the feldspathic type of Moor Grit. Both sericite and hydrobiotite are present as aggregates of minute flakes, the polarisation colours of which are of a lower order than those of muscovite.

Kaolin occurs in most of the rocks. It has a finely vermicular habit, and occurs as aggregates. A typical example is indicated in Fig. 52.

Limonite is not abundant, though it gives a brown colour to some of the samples. It is for the most part associated with the decomposition of secondary micas. It is conspicuous in Y7(b), as will be seen from Fig. 54, in which the black portions represent limonite.

Heavy Minerals.

R. H. Rastall (*loc. cit.*), followed by F. Smithson (*loc. cit.*), has emphasised the extraordinary abundance of zircon and the titania-bearing minerals and the relatively small proportion of other heavy minerals. The proportion of heavy minerals varies from 0.4% to 2%. The high proportion of titania-bearing minerals is shown in the analyses; for instance, Y8(b) contains 0.85% of titania.

The heavy-mineral assemblages show little variation. Zircon is rather more abundant in the fine-grained feldspathic rocks than in the coarser quartzitic rocks. The mineral species in the assemblages may be summarised as follows :

Zircon: Abundant; prismatic grains with rounded pyramidal terminations.

Rutile: Abundant; yellow-brown or reddish-brown irregular grains.

Tourmaline: Frequent; greenish-brown pleochroic rounded grains.

Brookite: Rare; rectangular yellow grains.

Ilmenite with *Leucocene*: Frequent; white or brown earthy grains.

Magnetite with *Limonite*: Frequent; brown magnetic grains.

Microstructure.

The microstructure of the Moor Grit varies considerably, and the following types may be distinguished:

(1) *Felspathic Moor Grit* in which the bond is due partly to sericite and kaolin and partly to the development of quartzitic structure. Fig. 51 shows a field in which the quartzitic structure holds many of the quartz grains together. Fig. 52 is a field in which kaolin and sericitic mica bond many of the quartz grains together; aggregates of grains with quartzitic structure may also be distinguished in this field. This microstructure is characteristic of Y1, Y2, Y4, Y6, Y11 and Y12. In Y7(b) the secondary micas have partly decomposed, with the consequent liberation of limonite, as shown in Figs. 53 and 54. Many of the grains are deeply corroded, and limonitic matter now fills the pits so formed, as shown in Fig. 54, in which the limonite is black and the quartz white.

When the rocks in which the bond is in part sericitic mica, kaolin or limonite are deeply weathered, these bonding minerals are removed, leaving the rock with an open texture and composed only of quartz together with a small amount of felspar. A typical field of a weathered specimen from locality Y11 is shown in Fig. 55.

(2) *Quartzitic Moor Grit* in which the bond is due to the development of quartzitic structure alone. The grain size may be variable, as in Fig. 56, in which a fine-grained band separates two medium-grained bands, or it may be uniform, as in Figs. 57 and 58. In each case the grain junctions are slightly corrugated and dovetail junctions are rare. This microstructure is characteristic of Y7(a), Y5, Y10 and Y13. The rock at locality Y3 is similar, but contains a small proportion of limonite.

(3) *Quartzitic Moor Grit* in which the bond is due to a mosaic of granular quartz. This structure is shown in detail in Fig. 61. The granular quartz is very fine-grained in Y8(a), as shown in Fig. 60, while in Y14 it is decidedly coarser, as in Fig. 59. The structure of Y8(b) is similar to that of Y8(a), but it is not quite so compact.

(4) *Quartzitic Moor Grit* which originally had the mosaic structure described under (3) above, but has since been ground by fault movements until a "mortar structure" has developed. This unusual structure is illustrated in Fig. 62, in which angular

or rounded quartz grains are set in a matrix of finely-divided quartz.

III.—CHEMICAL COMPOSITION.

The high silica content of the unwashed quartzitic Moor Grit is shown by the analyses recorded in Table XXII. They indicate that, with the exception of Y8(b), the only important mineral besides quartz is a clay mineral which is probably kaolin. The iron is present mainly as limonite. The low alkali content is particularly noteworthy.

TABLE XXII.—*Compositions of Unwashed Quartzitic Moor Grit.*

	Y3.	Y8(b).	Y9.	Y10.	Y13.	Y14.
SiO ₂ . % .	94.50	95.80	96.00	95.60	96.80	96.40
TiO ₂ . % .	0.26	0.85	1.59	0.35	0.34	0.71
Al ₂ O ₃ . % .	2.79	1.06	1.41	2.60	1.16	1.26
Fe ₂ O ₃ . % .	0.15	1.54	0.40	0.25	0.25	0.28
CaO. % .	0.05	0.05	0.00	0.10	0.00	0.05
MgO. % .	0.24	0.02	0.06	0.06	0.16	0.09
K ₂ O. % .	0.36	0.10	0.18	0.13	0.19	0.48
Loss. % .	1.25	0.70	0.45	0.70	0.55	0.30
Total. % .	99.60	100.12	100.09	98.94	99.45	99.57

IV.—THE MOULDING PROPERTIES OF THE CRUSHED ROCKS.

The rocks were first crushed in a small jaw-crusher and then milled lightly. This procedure was sufficient to separate most of the quartz grains in all but the most compact quartzites.

Mechanical Analyses.

The mechanical analyses of the crushed rocks are closely related to their microstructures. The felspathic and quartzitic types are best considered separately.

TABLE XXIII.—*Mechanical Analyses of Natural Moulding Sands.*

B.S.I. Sieve No.	F1.	F2.	F4.	F6.	F7(b).	F11.	F12.
On 5. % .	0.0	0.0	0.0	0.0	0.0	0.4	0.0
" 8. % .	0.1	0.0	0.1	0.7	0.8	2.5	0.5
" 10. % .	3.3	0.0	0.2	0.8	0.7	1.4	0.8
" 16. % .	7.2	0.0	1.9	6.7	3.1	4.8	8.1
" 22. % .	3.9	0.0	0.9	3.4	1.5	4.2	4.9
" 30. % .	3.5	0.7	1.1	2.7	2.4	8.9	4.2
" 44. % .	4.5	3.2	2.1	2.6	7.1	17.8	3.5
" 60. % .	5.0	9.0	16.3	5.3	28.1	25.8	3.5
" 72. % .	6.0	4.4	13.2	4.0	13.1	9.5	1.3
" 100. % .	17.9	23.4	36.9	25.5	22.2	15.2	3.7
" 150. % .	37.6	38.2	17.9	27.0	8.9	3.8	7.3
Thro' 150. % .	10.9	20.8	9.4	21.0	11.8	5.4	61.6
Total. % .	99.9	99.7	100.0	99.7	99.7	99.7	99.4

The mechanical analyses of the felspathic samples of Moor Grit are given in Table XXIII. The seven samples tabulated may be regarded as natural moulding sands, which in some cases could be improved by the addition of extra bond. The cumulative grading curves are given in Fig. 49.

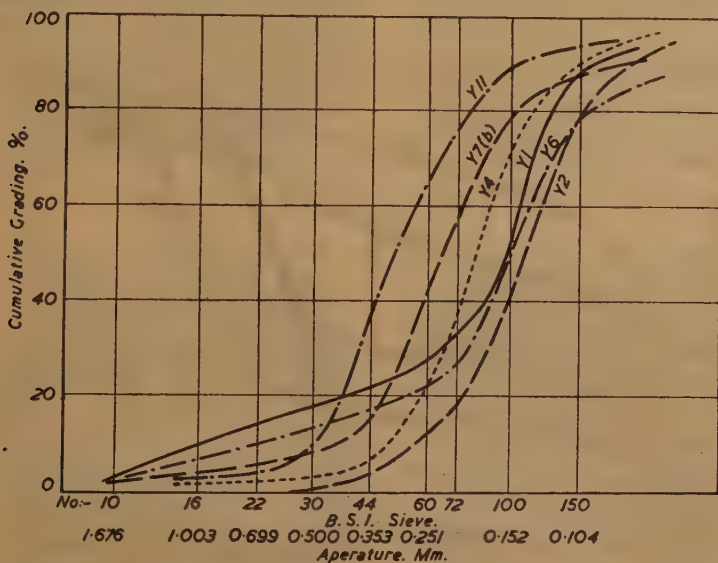


FIG. 49.—Cumulative Grading Curves for Natural Moulding Sands.

Y1, Y2, Y6 and Y3 are probably too fine-grained to be useful. Y4, Y7(b) and Y11 are not so fine-grained; Y11 is coarser than Chelford sand, while Y7(b) and Y4 are decidedly finer.

TABLE XXIV.—*Mechanical Analyses of High-Silica Sands before Washing.*

B.S.I. Sieve No.	Open Texture.					Compact Texture.			
	Y3.	Y5.	Y7(a).	Y8(b).	Y10.	Y8(a).	Y13.	Y14.	Y9.
On 5. %	0.0	0.0	0.0	0.0	0.0	24.7	3.1	13.3	29.4
" 8. %	0.1	0.2	0.0	1.4	0.0	17.5	11.9	11.7	24.6
" 10. %	0.1	0.1	0.0	1.2	0.0	4.1	3.1	3.1	5.1
" 16. %	0.6	0.8	0.5	5.5	0.0	8.9	5.5	7.0	12.3
" 22. %	0.4	0.6	0.6	2.5	0.0	2.9	1.2	2.0	4.0
" 30. %	0.6	1.2	1.8	3.3	1.7	3.0	0.9	1.6	3.6
" 44. %	2.6	6.1	7.0	5.3	3.8	3.9	0.9	2.0	3.4
" 60. %	27.1	29.6	24.6	23.5	12.9	5.1	2.1	4.9	3.3
" 72. %	21.3	13.9	13.3	11.2	6.5	8.6	1.3	2.7	1.3
" 100. %	29.3	25.4	33.7	21.2	16.7	7.4	8.9	9.5	3.1
" 150. %	9.8	10.7	9.2	7.6	21.5	4.3	35.6	15.8	2.4
Thro' 150. %	7.9	10.7	8.8	16.9	36.9	14.3	25.8	26.8	7.0
Total. %	99.8	99.3	99.5	99.6	100.0	99.7	100.3	100.4	99.5

The mechanical analyses of the quartzitic samples of Moor Grit are of two types, as will be seen from Table XXIV. and Fig. 50. This difference is dependent on the extent to which quartzitic structure of types 2, 3 and 4 (described above in Sub-Section II.) is developed. In samples in which quartzitic structure is not fully developed, the rock has an open texture and fracture occurs around the grains.

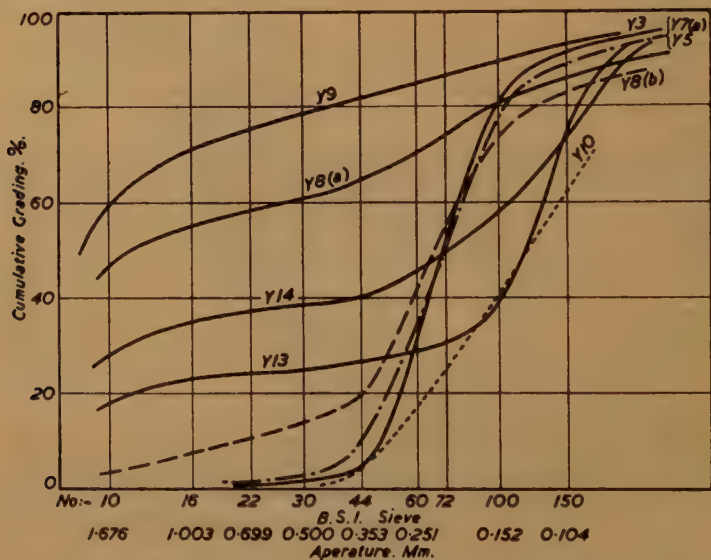


FIG. 50.—Cumulative Grading Curves for High-Silica Sands.

The grading of such rocks is largely governed by the size of the grains in the original rock, though, as mentioned in Sub-Section II., they tend to break during milling and so increase the proportion of the fines. Y8(b) contains a noteworthy proportion of finely granular quartz which acts as a bond; during milling, these granules are separated from each other, thus increasing the proportion of the fines.

In samples in which the quartzitic structure is fully developed, the rock has a compact texture; during crushing and milling it behaves as if it were homogeneous, and fracture occurs across instead of around the quartz grains. As a consequence, the crushed rock shows double grading, being composed of coarse angular rock fragments and finely-divided quartz with a very small proportion of medium-sized particles. This is particularly so in Y8(a) and Y14, which both contain a noteworthy proportion of granular quartz matrix. Y9 contains a high proportion of very finely-divided quartz, which tends to separate into its constituent particles during milling

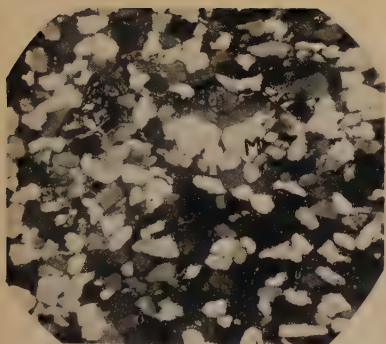


FIG. 51.—Y1. Felspathic Moor Grit; many grains held together by quartzitic structure. Grains of microcline felspar (*M*). × 30, crossed nicols.

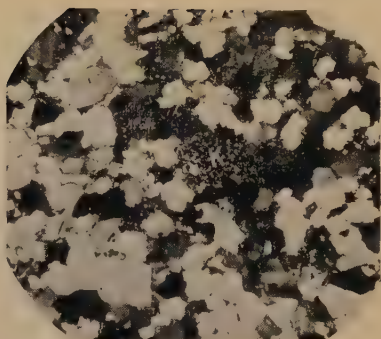


FIG. 52.—Y6. Felspathic Moor Grit; kaolin and sericitic mica bond many quartz grains together. Kaolin aggregate (*K*). × 30, crossed nicols.

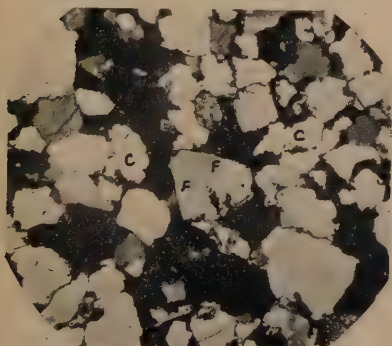


FIG. 53.—Y7(*b*). Felspathic Moor Grit, after weathering. Corroded grains (*C*), and development of secondary silica facets (*F*). × 30, crossed nicols.



FIG. 54.—Y7(*b*). The same field as Fig. 53. Distribution of limonite-stained sericite (black) between quartz grains (white). × 30, ordinary light.



FIG. 55.—Y11. Felspathic Moor Grit; sericitic mica and kaolin completely removed by weathering. × 30, crossed nicols.

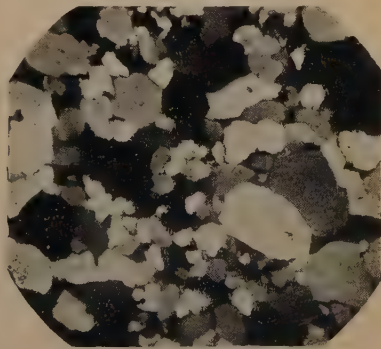


FIG. 56.—Y7(*a*). Quartzitic Moor Grit; wide range of grain size. × 30, crossed nicols.

(Micrographs reduced to four-fifths linear in reproduction.)

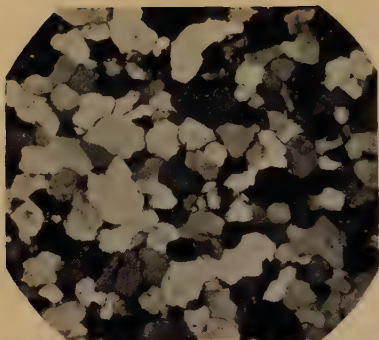


FIG. 57.—Y5. Quartzitic Moor Grit composed of grains of medium grade. $\times 30$, crossed nicols.

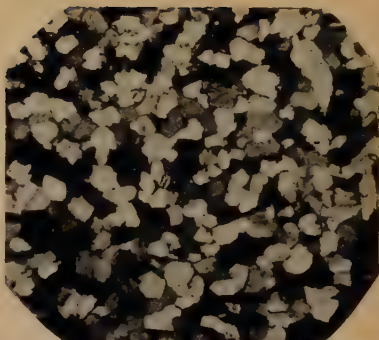


FIG. 58.—Y13. Quartzitic Moor Grit composed of grains of fine grade. $\times 30$, crossed nicols.

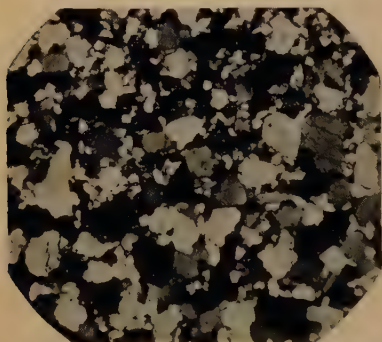


FIG. 59.—Y14. Quartzitic Moor Grit bonded by granular quartz of secondary origin. $\times 30$, crossed nicols.

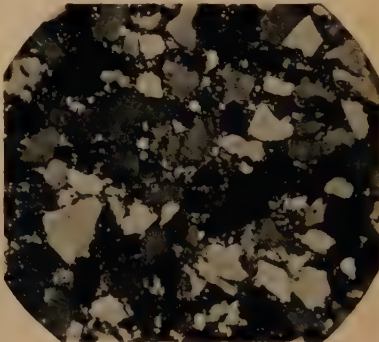


FIG. 60.—Y8(a). Quartzitic Moor Grit bonded by finely granular quartz of secondary origin. $\times 30$, crossed nicols.

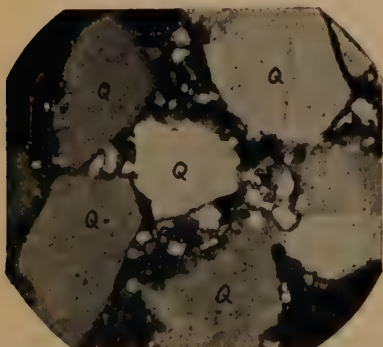


FIG. 61.—Y8(a). Detail of Fig. 60. Granular secondary quartz (S) between large quartz grains (Q). $\times 100$, crossed nicols.

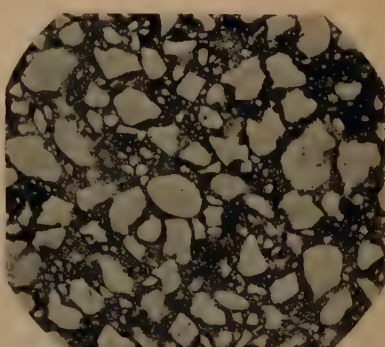


FIG. 62.—Y9. Quartzitic Moor Grit; "mortar-structure" due to fault movements. $\times 30$, ordinary light.

(Micrographs reduced to four-fifths linear in reproduction.)

and so increase the proportion of fines. The relative proportions of coarse and fine particles depend on the conditions of milling; as a rule prolonged milling increases the proportion of fines at the expense of the coarse fragments. While such a grading is useful for the manufacture of silica bricks, rocks with this compact texture will not yield the grading required for a high-silica steel-moulding sand.

Some of the coarser sands derived from the quartzitic rocks with open texture were washed, with the results given in Table XXV.

TABLE XXV.—*Mechanical Analyses of the Washed High-Silica Sands.*

Sand:	Y3.	Y5.	Y7(a).	Y8(b).	Arnold's 52.	Chelford.
Yield :	89%.	75%.	83%.	80%.
B.S.I. Sieve No.						
On 5. % .	0.0	0.0	0.0	0.0	0.0	0.0
" 8. % .	0.0	0.2	0.4	0.4	0.0	0.0
" 10. % .	0.2	0.3	0.4	0.4	0.2	0.0
" 16. % .	1.0	1.4	4.0	4.0	0.4	0.1
" 22. % .	0.6	0.8	2.8	2.6	0.9	0.3
" 30. % .	0.8	3.2	5.2	3.8	6.2	1.8
" 44. % .	3.2	8.0	12.4	6.8	37.5	10.2
" 60. % .	33.0	38.2	28.8	29.6	47.8	39.1
" 72. % .	21.6	17.6	13.8	13.6	5.0	22.0
" 100. % .	32.2	25.2	26.6	27.6	1.5	15.7
" 150. % .	6.6	4.0	5.4	8.4	0.5	8.3
Thro' 150. % .	1.4	0.6	1.0	3.2	0.1	2.6
Total. % .	100.6	99.5	100.8	100.4	100.2	100.1

Strength and Permeability.

(a) *Natural Moulding Sands.*—The natural bond of these sands is due to sericitic mica, kaolin and limonite; as will be seen from Table XXVI., this is sufficient to give the sands appreciable strength. For foundry work additional bond would probably be necessary in most cases. The test-pieces used were of A.F.A. dimensions and rammed by means of an A.F.A. rammer.

(b) *High-Silica Sands.*—These sands were bonded with ball clay; the results are given in Table XXVII. The strength and permeability of mixes of ball clay with Y5, Y7(a), Y8(b) and Y10 are in accord with their mechanical analyses. Thus Y8(b) and Y10 contain a higher proportion of fines than Y5 and Y7(a), and so their strength is greater and their permeability lower than those of Y5 and Y7(a).

Though Y3 is quartzitic, most of its grains have a thin coating of sericite. Consequently its strength is much higher than might be expected from a comparison of its grading and permeability with those of Y7(a).

TABLE XXVI.—*The Strength and Permeability of Natural Moulding Sands.*

	F1.	F2.	F4.	F6.	F7(b).	F11.	F12.
<i>A.—Test-Pieces of A.F.A. Dimensions Rammed 3 Times.</i>							
Moisture content. %	6	5	6	4	6	4	6
Weight of test-piece. G.	170	170	170	170	170	170	170
Max. green strength. Lb. per sq. in.	4.6	5.1	3.1	4.1	3.3	1.8	3.6
Permeability No.	37	42	70	32	85	170	18
Dry strength. Lb. per sq. in.	15	16	27	18	15	6	5
<i>B.—Test-Pieces of A.F.A. Dimensions Rammed 10 Times.</i>							
Moisture content. %	6	5	6	4	6	4	6
Weight of test-piece. G.	175	175	175	175	175	175	175
Max. green strength. Lb. per sq. in.	7.0	8.4	5.4	6.5	4.5	2.8	6.2
Permeability No.	28	32	48	22	60	130	14
Dry strength. Lb. per sq. in.	18	28	32	24	26	7	8

TABLE XXVII.—*The Strength and Permeability of High-Silica Sands Bonded with Ball Clay.*

	F3.	F5.	F7(a).	F8(b).	F10.
<i>A.—Test-Pieces of A.F.A. Dimensions Rammed 3 Times.</i>					
Ball clay. %	5	5	5	5	5
Moisture content. %	4	4	4	5	5
Weight of test-piece. G.	165	165	165	165	165
Green strength. Lb. per sq. in.	5.0	1.9	2.2	5.0	4.2
Permeability No.	110	115	125	40	40
Dry strength. Lb. per sq. in.	18	15	13	35	25
<i>B.—Test-Pieces of A.F.A. Dimensions Rammed 10 Times.</i>					
Ball clay. %	5	5	5	5	5
Moisture content. %	4	4	4	5	5
Weight of test-piece. G.	170	170	170	170	170
Green strength. Lb. per sq. in.	7.7	2.9	3.2	7.0	7.4
Permeability No.	90	85	90	32	27
Dry strength. Lb. per sq. in.	25	20	17	50	37

Refractoriness.

Test-pieces of A.F.A. dimensions, rammed three times, were prepared from mixes of the crushed rocks bonded with 5% of ball clay. These test-pieces were fired at 1550° C. for 2 hr. with the results indicated in Table XXVIII.

TABLE XXVIII.—*Refractoriness.*

Bonded with 5% of ball clay and fired at 1550° C. for 2 hr.

Sand No.	Shrinkage. %.		Remarks.
	Length.	Diameter.	
(a) <i>Felspathic Type containing some Natural Bond.</i>			
Y1	10	10	White; surface completely glazed.
Y2	Dark grey; test-piece squatted; surface completely glazed.
Y4	10	5	Grey; surface glazed.
Y6	Brown; test-piece squatted; surface completely glazed.
Y7(b)	10	10	Brown; surface glazed.
Y11	5	5	Pale brown; grains slightly glazed.
Y12	Test-piece completely fused.
(b) <i>Quartzitic Type.</i>			
Y3	0	2.5	White; grains very slightly glazed.
Y5	0	0	White; grains very slightly glazed.
Y7(a)	0	0	White; grains very slightly glazed.
Y8(b)	0	0	Brown; grains slightly glazed.
Y10	10	10	Grey; surface fritted; test-piece badly crushed.

V.—CONCLUSIONS.

In the Moor Grit exposures which are reasonably accessible some of the lithological varieties are suitable for use as steel-moulding sands. In particular, the coarser felspathic varieties could be used as natural moulding sands, though in most cases the addition of bond is desirable.

Quartzitic varieties having an open texture can be crushed easily to yield a high-silica sand suitable for steel-moulding work.

Quartzitic varieties having a compact texture are of little interest for steel-moulding purposes, for their grading after crushing is unsuitable.

APPENDIX.—*Local Details of the Moor Grit Exposures.*

To avoid repetition, the reader is referred to Sub-Section II. for the detailed descriptions of the mineral constituents other than quartz. In the following petrological descriptions, only the relative proportions of these minerals have been noted.

Y1, *Felspathic Type.*

Situation.—Roadside exposure at Hazel Heads, 4 miles north-north-west from Helmsley Station.

Petrological Description.

The rock exposed at this locality is a fine-grained, fairly compact, felspathic sandstone, pale brown in colour. Angular quartz grains,

0.1–0.2 mm. across, form the bulk of the rock; the remainder is composed of equal proportions of muscovite, fresh microcline, sericitic mica and kaolin. The quartz grains contain scattered inclusions and are free from strain. Nearly all of them are corroded and crystal facets are uncommon. The quartz grains are only partly in contact; their junctions are slightly corrugated but never interlocking.

The heavy-mineral assemblage forms 0.5% of the sample. The quartz grains can be separated by crushing followed by light milling.

Y2, Felspathic Type.

Situation.—Disused quarry at Solomon's Temple, 1½ miles east of Osmotherly. The nearest railway station is at Potto, about 5 miles away by road.

Petrological Description.

Felspathic brown Moor Grit, having a fairly open texture, is exposed at this locality. Many of the quartz grains have developed crystal facets, which make the rock sparkle. The bulk of the rock is composed of quartz grains together with a small portion of quartzite grains; the grain size varies between 0.25 and 0.50 mm., and many of the quartz grains are crushed and contain linearly arranged inclusions. Fresh microcline and sericitic mica are the only other important constituents. Quartzitic structure is not well developed; where the grains are in contact, the junction is slightly corrugated. Most of the grains adjoining pores have developed crystal facets.

The heavy-mineral assemblage forms 0.4% of the sample. The quartz grains can be separated by crushing and light milling. Though the average grain size of this rock is at least twice that of Y1, the grading of the crushed rock is finer than that of Y1, because the quartz grains in Y2 fracture along incipient cracks and weaknesses due to inclusions.

Y3, Quartzite Type.

Situation.—Roadside exposure at Vear Moor, 1½ mile north-east of Osmotherly; 5 miles by road from Potto Station.

Petrological Description.

The sandstone at this locality has an open texture and varies from brown to grey in colour. Except for one or two grains of quartzite and fresh microcline, it is composed of angular quartz grains, 0.2–0.4 mm. across, enclosing a few scattered bubble inclusions and partly coated with limonite-stained sericitic mica. Many of the grains have been deeply pitted by corrosion, while others have well-developed crystal facets. The rock has a quartzitic microstructure in which the grains are separated by a thin film of sericitic mica.

The heavy-mineral assemblage forms 0.7% of the rock. The grains are easily separated by light milling, yielding a sand the grain size of which ranges from 0.35 to 0.15 mm.; the silica content of the unwashed sand is 94.5%. The yield of washed sand is 89%.

Y4, Felspathic Type.

Situation.—Disused freestone quarry at Black Shire, 1½ mile north-north-east of Osmotherly; 5 miles by road from Potto Station.

Petrological Description.

Pale-brown, even-grained sandstone, having a fairly open texture, is exposed in this quarry. The greater part of the rock is composed of quartz grains, 0.15–0.30 mm. across, which have been deeply fritted by corrosion; few of the grains have a layer of secondary silica. Most of the quartz grains contain scattered inclusions only. Quartzite grains are rare. The other mineral constituents are fresh microcline, kaolin, sericitic mica, limonite and a few flakes of muscovite. Corrosion and, to a less extent, the deposition of secondary silica have brought about some accommodation of grain shape. Owing to the amount of sericitic mica and kaolin distributed through the rock, quartzitic structure is poorly developed, and these two minerals form much of the bond between the quartz grains.

The heavy-mineral assemblage forms 0.5% of the rock. The quartz grains can be separated by crushing followed by light milling.

Y5, Quartzitic Type.

Situation.—Moorland exposure adjoining the Castleton/White-Cross road, $\frac{1}{2}$ mile north-north-west of Castleton Station.

Petrological Description.

The rock exposed at this locality is white or stained slightly by brown limonite. Over most of the exposure, it has the appearance of lump sugar, owing to its open texture and the extensive development of crystal facets on the quartz grains. A small part of the exposure has a compact texture. Except for one or two small pockets of kaolin, the rest is composed of quartz together with a few grains of quartzite. The majority of the quartz grains are 0.15–0.30 mm. across and contain scattered inclusions. A small proportion of quartz is granular and of secondary origin. Quartzitic structure is fairly well-developed, but the grains are only partly in contact. The junctions are slightly corrugated but not interlocking.

The heavy-mineral assemblage forms 0.5% of the rock. The open-textured variety can be separated into its constituent grains by light milling, but the compact variety has to be crushed before the grains will separate. The yield of washed sand is 75%.

Y6, Felspathic Type.

Situation.—Disused quarry adjoining the Castleton/White-Cross road, $\frac{1}{4}$ mile north-west of Castleton Station.

Petrological Description.

Pale brown, fairly compact freestone is exposed in this quarry. Crystal facets are conspicuous in most of the quartz grains. The rock is composed of quartz, quartzite, microcline feldspar, sericitic mica, kaolin and a little limonite. Some of the quartz grains are fritted by corrosion, while others have developed crystal facets. Most of the quartz grains contain scattered inclusions. The grain size ranges from 0.1 to 0.3 mm. Some of the quartz grains form quartzitic aggregates with simple sutures, but many of the grains are set in a matrix of sericitic mica, kaolin and limonite.

The heavy-mineral assemblage forms 0.4% of the rock. The quartz grains can be separated by crushing followed by milling.

Y7(a), Quartzitic Type.

Situation.—New Top quarry at the quarries of General Refractories, Ltd., adjoining Castleton Station.

Petrological Description.

A white, or pale-brown, sandstone, having an open texture, is exposed at this quarry. Crystal facets are extensively developed on the quartz grains. The rock has a finely-banded appearance, due to alternation of fine- and medium-grained layers. At present the rock is won for silica-brick manufacture elsewhere. The browner parts, which are not suitable for this purpose, could be employed as high-silica sand for steel moulding.

Except for one or two small pockets of kaolin, the rock is composed entirely of quartz grains together with a few grains of quartzite. The quartz contains scattered inclusions. The grains in the finer bands are about 0.15 mm. across, while those in the coarser bands are 0.25–0.4 mm. across. Quartzitic structure is not well-developed; where the grains are in contact the junction is slightly corrugated.

The heavy-mineral assemblage forms 0.5% of the rock. The quartz grains can be separated by light milling. The yield of washed sand is 83%.

Y7(b), Felspathic Type.

Situation.—Bottom quarry at the quarries of General Refractories, Ltd., adjoining Castleton Station.

Petrological Description.

This quarry is worked for natural moulding sand. The rock is a brown, fairly compact, felspathic sandstone; crystal facets are developed on many of the quartz grains.

Quartz grains form the bulk of the rock, the other important mineral constituents being rather decomposed microcline, sericitic mica, kaolin and limonite. Most of the quartz is present as simple grains 0.15–0.3 mm. across, though a small proportion is present as quartzite grains. Many of the quartz grains contain linearly arranged inclusions and are fractured. Corrosion and the development of crystal facets have given the grains deeply-pitted and angular surfaces, respectively. Though the bond of the rock is in part due to the development of quartzitic structure, sericitic mica, kaolin and limonite form an important part of the bond.

The heavy-mineral assemblage forms 0.4% of the rock. Jaw-crushing followed by light milling separates the quartz grains fairly easily.

Y8, Quartzitic Type.

Situation.—Doubting Castle Quarry, owned by General Refractories, Ltd., $\frac{1}{4}$ mile north of Danby Station.

Petrological Description.

Two varieties of quartzitic Moor Grit are exposed in this quarry. The first, which is won for silica-brick manufacture, is a compact white quartzite the fractured surfaces of which have a glassy appearance. The second variety is not so compact and exhibits brown mottling due to limonite staining; many of the grains have developed crystal facets. This variety is regarded as waste at present.

Both varieties are composed almost entirely of quartz; the second

contains a small proportion of limonite. The original quartz grains are 0.2–0.3 mm. across and contain scattered inclusions; some of the grains have undulose extinction. Grains of quartzite are rare.

Besides these original quartz grains, there is much granular quartz of secondary origin; these granules rarely exceed 0.2 mm. in dia. Though some of the original quartz grains are arranged in typical quartzitic structure, the majority are set in a matrix of granular quartz, which thus acts as the main bond of the rock.

The heavy-mineral assemblage forms 1.3% of the rock. The compact variety is extremely resistant to crushing and milling, but the less compact variety is easily broken down by crushing and milling.

Y9, Quartzitic Type.

Situation.—Clitherbeck Quarry, owned by General Refractories, Ltd., $\frac{3}{4}$ mile north-north-east of Danby Station.

Petrological Description.

This rock is unusual. It was originally Moor Grit of the quartzite type; it has, however, been involved in fault movements, with the result that it has been crushed and subjected to grinding action. Now the rock is composed of isolated quartz grains, or clusters of grains, set in an extremely fine-grained matrix of silicified quartz flour. The rock is at present being won for silica-brick manufacture elsewhere. Under the microscope it exhibits typical mortar-structure, that is, a structure characteristic of rocks that have been disturbed by fault movements. Most of the quartz grains have undulose extinction due to permanent strain. The largest quartz grains are 0.4 mm. across.

The heavy-mineral assemblage forms 2% of the rock—an extraordinarily high proportion. The rock is extremely difficult to crush.

Y10, Quartzitic Type.

Situation.—Roadside exposure at Spindle Thorn, 2 miles north-north-east of Hutton-le-Hole.

Petrological Description.

This rock is a pale-brown, fine-grained quartzite, which breaks into flakes when struck.

Apart from a very small proportion of sericitic mica and kaolin, the rock is composed entirely of quartz grains, most of which are 0.1–0.2 mm. across, though a few are as much as 0.4 mm. across. The grains contain a few scattered inclusions and are free from strain. Quartzitic structure, in which the grain junctions are slightly corrugated, is well developed.

The heavy-mineral assemblage forms 0.8% of the rock. Crushing and milling will separate most of the quartz grains. The yield of washed sand is 55%.

Y11, Felspathic Type.

Situation.—Roadside exposure above Lowna, 1 mile north-north-east of Gillamoor, 4 miles by road from Kirby Moorside Station.

Petrological Description.

Pale-brown felspathic sandstone, having a fairly open texture, is exposed at this locality. Few of the quartz grains have developed crystal facets.

The bulk of the rock is composed of quartz grains together with a

few quartzitic grains; sericitic mica, kaolin and a little microcline are the other important mineral constituents. The quartz grains range from 0.2 to 0.5 mm. across. The majority are unstrained and contain scattered inclusions. Some of the grains are pitted by corrosion, while others have an irregular coating of secondary mica. The bond of the rock is due in part to the development of quartzitic structure and in part to the sericitic mica and kaolin.

The heavy-mineral assemblage forms 1.0% of the rock. The quartz grains are readily separated by crushing followed by light milling.

Y12, Felspathic Type.

Situation.—Roadside exposure at Hazel Green, 2½ miles north of Helmsley Station.

Petrological Description.

This rock is a very fine-grained, compact felspathic sandstone. It is composed of quartz, some microcline and abundant limonite-stained sericitic mica and kaolin. Small muscovite flakes occur on the bedding planes. The quartz grains are nearly all of silt grade and are deeply fritted by corrosion. Aggregates of quartz grains with quartzitic structure are set in a matrix of sericitic mica and kaolin.

The heavy-mineral assemblage forms 0.9% of the rock. The quartz grains are not easily separated by crushing and milling. Many aggregates of quartz grains survive prolonged milling.

Y13, Quartzitic Type.

Situation.—Disused quarry at Old Fold, 2 miles north of Helmsley Station.

Petrological Description.

Fine-grained compact quartzite is exposed in this quarry; except for a small amount of limonite-staining, it is white. Apart from a small proportion of kaolin and sericitic mica, the rock is composed entirely of quartz grains, most of which show undulose extinction and contain scattered inclusions. The grains are 0.15–0.25 mm. across. Quartzitic structure is well developed and the grains boundaries are slightly corrugated.

The heavy-mineral assemblage forms 0.7% of the rock. The rock is extremely resistant to crushing.

Y14, Quartzitic Type.

Situation.—Moorland exposure at Old Fold, 2 miles north of Helmsley.

Petrological Description.

This rock is best described as a compact white quartzite, which fractures across the grains rather than round them; some of the fractured surfaces have a glassy appearance.

Apart from an unusually high proportion of titania-bearing heavy minerals and a small proportion of sericite and kaolin, the rock is composed entirely of quartz grains which are unstrained and contain a few scattered inclusions. The original quartz grains are 0.15–0.25 mm. across. There is a noteworthy proportion of quartz granules 0.05 mm. in dia. The bond is in part a quartzitic one in which the large grains have slightly corrugated contacts with each other, and in part one in which large grains or quartzitic aggregates of large grains are joined together by a mosaic of quartz granules.

The heavy-mineral assemblage forms 1.0% of the rock. The rock is extremely resistant to crushing.

PART 4.—THE ROTTEN-ROCK MOULDING SANDS ABOUT WOLSHINGHAM, CO. DURHAM.¹

(Fig. 65 — Plate IX.)

SUMMARY.

These friable sandstones are extensively worked for the production of naturally-bonded moulding sands for use in the steel foundries of Tees-side and Tyneside and elsewhere. This paper is a preliminary one and describes the bonding properties of some of these sands. Attention is directed to the importance of the mineral constitution of the bond; it is indicated that a hydrobiotite bond is preferable to a sericite bond.

I.—INTRODUCTION.

The positions of the rotten-rock quarries are indicated on the sketch map, Fig. 63. The geological horizon of the Viewley Hill



FIG. 63.—Sketch Map indicating the Localities Examined.

¹ Received November 2, 1942.

Quarry is near the top of the Millstone Grit Series; the other quarries are at horizons close to the base of this Series.

II.—LOCAL DETAILS.

W1, *Parkhead Quarry (Messrs. Durhill's, Ltd., Stanhope).*

A face about 20 ft. high is being worked in this quarry. The rock exposed is false-bedded; consequently the geological section varies from point to point along the face as one lens of the false-bedding thins out and another appears. The section shown in Fig. 64 is fairly representative. Within each sandstone lens the

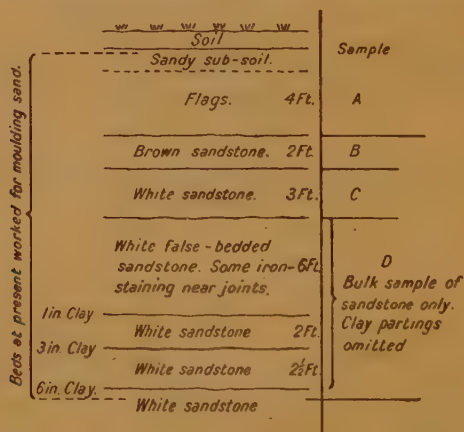


FIG. 64.—Section at Parkhead Quarries.

grain size varies from coarse at the base of the lens to medium or even fine at the top of the lens. Between some of the sandstone lenses are partings, $\frac{1}{2}$ in. to 6 in. thick, of iron-stained, silty clay. These partings are lenticular; the largest seen was 6 in. thick and extended for only 30 ft. along the face. The clay partings are worked along with the sandstone and add considerably to the bond of the milled sand.

The mechanical gradings of the four samples *A*, *B*, *C* and *D* (see Fig. 64) are similar, though *A* contains rather more material finer than B.S.I. 150-mesh than the other samples. The mechanical gradings are shown in Table XXIX.

The moulding properties of the four samples are summarised in Table XXX. There is a continuous variation in the properties from the top (*A*) to the bottom (*D*) of the face. For a given moisture content, both the green and dry strengths increase while the permeability coefficient decreases from the top to the bottom of the face. This variation is due to weathering by the leaching action of water

TABLE XXIX.—*Mechanical Gradings of the Rotten-Rocks.*

B.S.I. Sieve No.	W1. Parkhead Quarry.				W2, W3. Waskerley Quarries.		
	A.	B.	C.	D.	W2.	W3.	X.
On 5. % .	0.0	0.0	0.0	0.1	0.0	0.0	0.0
„ 8. % .	0.1	0.2	0.1	0.5	0.1	0.4	0.0
„ 10. % .	0.2	0.3	0.1	0.2	0.4	0.6	0.0
„ 16. % .	5.2	11.2	12.0	10.5	20.1	18.4	6.4
„ 22. % .	5.0	7.5	9.0	7.6	11.5	14.2	6.5
„ 30. % .	10.3	12.1	12.2	10.7	11.6	16.7	10.5
„ 44. % .	24.7	27.8	18.3	16.5	14.6	20.9	13.7
„ 60. % .	25.5	24.6	23.8	22.6	17.6	13.4	20.7
„ 72. % .	4.4	5.3	5.9	5.6	4.4	2.3	7.4
„ 100. % .	9.6	9.1	9.4	13.0	9.6	4.5	18.9
„ 150. % .	5.6	5.1	4.4	6.6	4.5	3.3	9.3
Thro' 150. %	9.2	6.7	4.6	6.1	5.6	5.2	6.4
Total. % .	99.8	99.9	99.8	100.0	100.0	99.9	99.8

B.S.I. Sieve No.	W4. Dead Friars Quarry.		W5. Weather Hill Quarry.	W6. Harperley Hill Quarry.	W7. Viewley Hill Quarry.
	Main Face.	Right Face.			
On 5. % .	0.0	0.0	0.0	0.0	0.0
„ 8. % .	0.2	0.1	0.1	0.5	0.2
„ 10. % .	0.6	0.2	0.1	2.6	0.4
„ 16. % .	6.6	21.7	4.4	17.4	17.2
„ 22. % .	7.4	15.9	7.0	25.8	9.6
„ 30. % .	14.4	17.4	11.4	13.2	12.0
„ 44. % .	21.9	16.4	18.4	14.8	16.8
„ 60. % .	21.3	14.3	24.6	10.9	19.8
„ 72. % .	4.9	2.8	5.5	2.0	4.4
„ 100. % .	9.4	4.4	10.1	4.4	7.9
„ 150. % .	5.6	2.6	5.7	3.4	4.6
Thro' 150. %	7.5	4.1	12.7	4.9	6.9
Total. % .	99.8	99.9	100.0	99.9	99.8

TABLE XXX.—*Moulding Properties of the Parkhead Samples.*

Test-pieces of A.F.A. dimensions; rammed 10 times.

	For an Approx. Moisture Content, %, of—	Sample A (Top).	Sample B.	Sample C.	Sample D (Bottom).
Permeability No. {	6.0	66	55	40	23
Max. green strength. {	7.75	81	46	33	16
Lb. per sq. in. {	6.0	12.7	13.7	18.5	20.7
Dry strength. Lb. {	7.75	8.7	12.5	13.6	19.1
per sq. in. {	6.0	90	119	145	176
	7.75	100	127	161	220

which has percolated through the peaty soil and reacted with the bond of the rotten-rock.

Sample *A* includes as much of the sandy sub-soil as is usually worked for moulding sand. This sub-soil has been subject to mechanical as well as chemical weathering, whereby some of the quartz grains constituting the sand grade have been broken down to silt. Consequently the proportion of material finer than 150-mesh is higher than in the other samples, though it actually contains less clay grade. This is confirmed by the permeability coefficients; that for sample *A* increases with the addition of water, while those of samples *B*, *C* and *D* decrease. This is because the clay in samples *B*, *C* and *D* swells and tends to fill the pores, thereby decreasing the permeability, whereas the silt grains, within limits, increase the permeability as the moisture content is increased.

Samples *A*, *C* and *D* are white, except for localised reddish-brown staining due to limonite, particularly near the joints. Sample *B* is brown and contains an appreciable amount of limonite. The bond of sample *B* includes some hydrobiotite, while samples *A*, *C* and *D* contain little or none of this mineral. Few muscovite flakes can be found in any of the samples; their effect on the moulding properties will be negligible.

The variation in moulding properties from the top to the bottom of the face is greater than might be expected from macroscopic examination; it may be noted that the Millstone Grits of the Peak District have better moulding characteristics in the unweathered than in the weathered state. The moulding characteristics of the milled sandstone from Parkhead Quarry might be improved in two ways: First, the thickness of material rejected as overburden should be increased so as to include most of the flags constituting sample *A*; by rejecting this poorly-bonded material, the moulding characteristics of the milled rock should be improved. Secondly, there seems to be no reason why the quarry should not be deepened so as to include beds below those at present worked; in this way more moulding sand could be won for the removal of a given thickness of overburden.

W2, W3, Wakerley Quarries (Messrs. Durhill's, Ltd., Stanhope).

A sample from the small trial hole at *W2* was examined; this locality can scarcely be described as a quarry. Long-since disused workings, at the most 5 ft. deep, are situated a few yards from the railway. No solid rock can be seen and the site will have to be reopened as if no quarry had ever existed. Furthermore, the site is rather low-lying, and drainage troubles will certainly be encountered. The moulding characteristics of a second sample from the same trial hole are given in Table XXXI.; they are not so promising as those of the earlier sample. The trial hole is so shallow that both samples were taken from the sub-soil only and do not give information about the properties of the underlying rock. This is

emphasised in Table XXIX.; *X* represents the grading at a point 15 yards away from the trial hole *W2*.

About 150 yards away is a disused quarry (*W3*, Fig. 63), in which 10 ft. of sandstone, closely resembling the white sandstone of Parkhead Quarry, is exposed. The moulding characteristics of this rock are given in Tables XXIX. and XXXI.

W4, Dead Friars Quarry (Mr. J. J. S. Wilkinson, Blanchland).

False-bedded, rather chloritic sandstone is exposed in the main face, about 15 ft. high, at this quarry. To the right of this face is a second smaller face, working a sandstone containing little or no chloritic matter. The mechanical grading and moulding characteristics are given in Tables XXIX. and XXXI. The main face yields a stronger moulding sand than the right face. A further bulk sample representative of the quarry output had the same characteristics as the sample collected from the main face.

W5, Weather Hill Quarry (Mr. Hobson). (Output taken by General Refractories, Ltd.).

This quarry is rather shallow, and the sandstone at present worked resembles the upper part of the Parkhead section. The uncrushed rock is sent by rail to Rowley Station, where it is crushed by very light, electrically-driven mills. Its moulding characteristics lie between those of samples *A* and *B* from Parkhead Quarry, as will be seen from Table XXXI. The mechanical grading is recorded in Table XXIX.

W6, Harperley Hill Quarry (General Refractories, Ltd.).

The sandstone at this quarry is similar to, though more iron-stained than, the Parkhead sample *D*. The stone is taken by lorry to Wolsingham, where it is milled and put on rail. Although its grading is slightly coarser than the sample *D*, its dry strength is rather better (see Tables XXIX. and XXXI.).

W7, Viewley Hill Quarry (Mr. Thompson).

The rock at this locality is overlain by some 12–15 ft. of glacial drift. The base of the rotten-rock is not exposed, and at present the thickness of rotten-rock being worked is about 15 ft. The moulding characteristics of the crushed rock are particularly good, as will be seen from Table XXXI. The mechanical grading is given in Table XXIX.

III.—THE PETROLOGY OF THE ROTTEN-ROCKS.

Microscopic examination shows that the rotten-rocks are all of the same type. Essentially they are composed of angular quartz grains bonded together by micaceous minerals. A small proportion of the grains interlock so as to form quartzitic aggregates. Fig. 65

TABLE XXXI.—*Moulding Properties of the Rotten-Rocks.*

Bulk rock samples crushed and milled in the Refractories Department, Sheffield University.
All test-pieces of A.F.A. dimensions; rammed 10 times.

W1. Parkhead Quarry.										W2, W3. Waskenley Quarries.									
A.		B.		C.		D.		W2.		W3.									
Moisture content.	%	7.6	6.1	7.6	5.7	7.6	6.1	7.8	5.8	7.5	5.8	7.7							
Bulk density		1.67	1.69	1.72	1.69	1.72	1.71	1.75	1.75	1.79	1.71	1.75							
Permeability No.		66	81		40	33	23	16	15	12	53	60							
Green strength.	Lb.																		
per sq. in.		12.7	13.7	12.5	18.5	13.6	20.7	19.1	21.3	21.0	19.4	13.0							
Dry strength.	Lb. per																		
sq. in.		90	119	127	145	161	176	220	123	157	98	118							
W4. Dead Eriars Quarry.										W5. Weather Hill Quarry.									
		Main Face.		Right Face.						W6. Harperley Hill Quarry.		W7. Viewley Hill Quarry.							
Moisture content.	%	6.7	8.6	6.2	7.7	7.9	6.5	7.9	6.1	7.8	5.7	8.2							
Bulk density		1.71	1.75	1.73	1.75	1.75	1.71	1.75	1.71	1.75	1.75	1.79							
Permeability No.		38	32	40	32	36	39	36	55	50	19	18							
Green strength.	Lb. per sq. in.	21.3	19.7	21.0	13.4	12.1	12.6	12.1	21.2	19.6	28.3	25.8							
Dry strength.	Lb. per sq. in.	179	189	142	144	102	78	102	229	295	403	433							

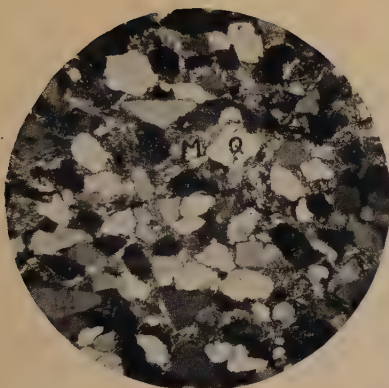


FIG. 65.—Microstructure of a Typical Rotten-Rock before Crushing, showing quartz grains (*Q*) set in a micaceous matrix (*M*). $\times 30$.

[*Davies & Rees (Part 4).*

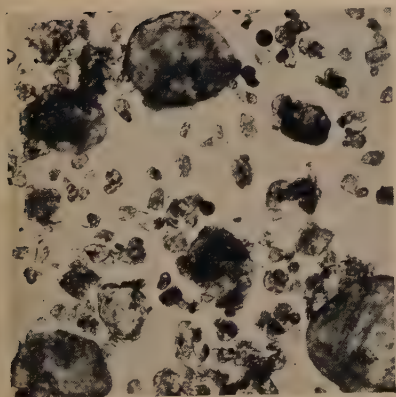


FIG. 66.—Crime Rigg Bottom. $\times 30$.

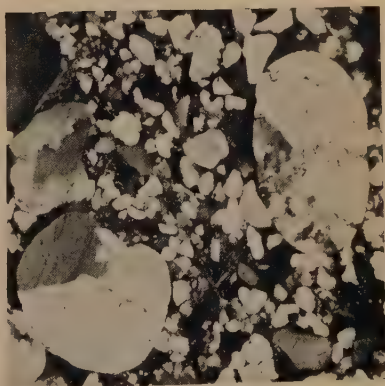


FIG. 67.—Crime Rigg Bottom. $\times 30$, crossed nicols.

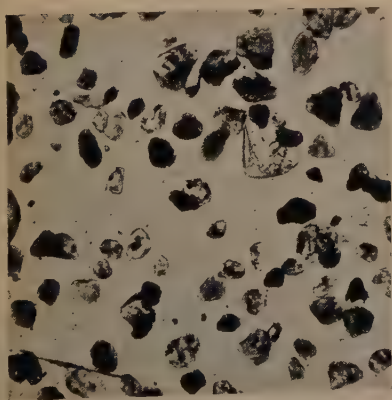


FIG. 68.—Pontefract. $\times 30$.

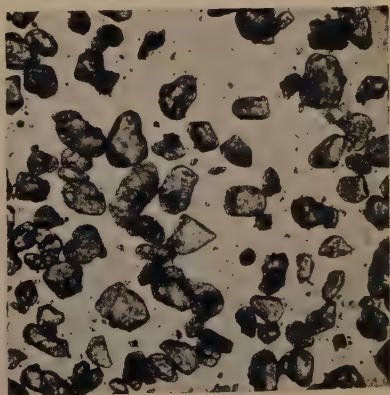


FIG. 69.—Castleton Road End. $\times 30$.

(Micrographs reduced to four-fifths linear in reproduction.)

[*Davies & Rees (Part 5).*
[To face p. 102 F.

illustrates the typical microstructure; the micaceous minerals forming the bond are indicated by *M*, while the quartz grains are indicated by *Q*.

The nature of the micaceous minerals is of great importance, for it controls the moulding properties. Consider the green strength figures given in Table XXXI.: The maximum green strength is obtained for a moisture content of 5.5–6.5%; when the moisture content is increased by a further 2%, the green strengths of some of the samples decrease sharply, while those of the remaining samples decrease but slightly. The data are rearranged in Table XXXII. to emphasise this point.

The micaceous minerals constituting the bond of the rotten-rocks are of two types—hydrobiotite and sericite. The former contains a variable proportion of iron, while the latter contains practically no iron. They are readily distinguished microscopically, for the hydrobiotite micas have a dull green colour, which deepens as the iron content increases; the sericite micas, on the other hand, have a pale brown colour.

In Table XXXII., Parkhead *C*, Waskerley *W3* and Dead Friars right face give green strengths typical of the sericite micaceous bonds; in Parkhead *A*, the bond is weathered to a greater extent and so is not as efficient.

In the hydrobiotite group in Table XXXII., Viewley Hill gives an outstandingly high green strength; the hydrobiotite mica forming its bond is so rich in iron that it imparts a green colour to the rock. The hydrobiotite micas forming the bond of Harperley Hill, Dead Friars main face, Waskerley *W2* and Parkhead *D* are not so rich in iron and their green strengths are correspondingly

TABLE XXXII.—*Green Strengths of the Rotten-Rocks.*

Sample.	Green Strength. Lb. per sq. in.		
	At 6% Moisture.	At 8% Moisture.	Percentage Decrease.
<i>Sericite Group.</i>			
<i>W1</i> , Parkhead <i>A</i> . . .	12.7	8.7	31.5
<i>W1</i> , Parkhead <i>C</i> . . .	18.5	13.6	26.4
<i>W3</i> , Waskerley . . .	19.4	13.0	33.0
<i>W4</i> , Dead Friars, right face .	21.0	13.4	36.2
<i>Hydrobiotite Group.</i>			
<i>W5</i> , Weather Hill . . .	12.6	12.1	4.0
<i>W1</i> , Parkhead <i>B</i> . . .	13.7	12.5	8.8
<i>W1</i> , Parkhead <i>D</i> . . .	20.7	19.1	7.7
<i>W2</i> , Waskerley . . .	21.3	21.0	1.4
<i>W4</i> , Dead Friars, main face .	21.3	19.7	7.5
<i>W6</i> , Harperley Hill . . .	21.2	19.6	7.6
<i>W7</i> , Viewley Hill . . .	28.3	25.8	8.9

lower. The bond in Weather Hill and Parkhead *B* is weathered to a greater extent; consequently the green strengths are low by comparison.

IV.—CONCLUSION.

Rotten-rocks which can be milled to produce moulding sands suitable for use in steel foundries are widely distributed in this district near Wolsingham. The relation of the moulding characteristics to the constitution of the minerals forming the bond is stressed, and it is shown that a hydrobiotite bond is preferable to a sericite bond.

PART 5.—THE PERMIAN YELLOW SANDS OF DURHAM AND YORKSHIRE.¹

(Figs. 66 to 69 — Plate IX.)

SUMMARY.

These sands have been exploited for use as iron-moulding sands, but they have rarely been employed for steel-moulding, as many of the occurrences are not sufficiently refractory. It is possible that the more refractory occurrences included in this account could be utilised in steel-moulding sands with the addition of bonding clay.

I.—INTRODUCTION.

The Permian Yellow Sands have not been used extensively for moulding purposes. They have been exploited at Pontefract and Castleford for iron-moulding sand and at Laughton-en-le-Morthen (east of Sheffield) for non-ferrous founding. P. G. H. Boswell² says that the sands "are often incoherent, but are too deeply iron-stained and calcareous all along their outcrop to be of service" as high-silica sands, and he notes their use as iron-moulding sands. M. B. Hodge³ and H. C. Versey⁴ have described the geology of the sands in Durham and in Yorkshire, respectively.

The outstanding feature of many of the sands is their double grading. These double-graded sands are composed of fine grains 0.05–0.15 mm. across and coarse grains about 0.50 mm. or more across. The relative proportions of the two grades vary from exposure to exposure, and at some localities the coarser grade is

¹ Received November 3, 1942. Mr. W. Anderson, M.Sc., of H.M. Geological Survey, collaborated in this investigation, and reference may be made to the Geological Wartime Pamphlet No. 31 on "Some Refractory Materials in North-East England," by R. G. Carruthers and W. Anderson.

² "A Memoir on British Resources of Refractory Sands," pp. 201, 204. London, 1918: Taylor and Francis.

³ "The Permian Yellow Sands of North-East England," *Proceedings of the University of Durham Philosophical Society*, 1927–32, vol. 8, pp. 410–458.

⁴ "The Beds Underlying the Magnesian Limestone in Yorkshire," *Proceedings of the Yorkshire Geological Society*, 1923–26, vol. 20, pp. 200–212.

absent. This double grading was first described by Hodge. It is the grading rather than the chemical or the mineralogical constitution that controls the moulding properties of these sands.

The sands were obtained from the following localities :

Sherburn Hill: Quarry $\frac{1}{2}$ mile east of Sherburn Hill, $3\frac{1}{2}$ miles east of Durham.

Hetton Downs: Quarry $\frac{1}{2}$ mile north-east of Hetton-le-Hole, 6 miles north-east of Durham.

Coxhoe: Quarry $\frac{3}{4}$ mile east of Coxhoe, 5 miles south-east of Durham.

Downhill: Quarry $\frac{3}{4}$ mile south of West Boldon.

Crime Rigg: Quarry $\frac{1}{2}$ mile south-east of Sherburn Hill.

Ferryhill: East side of railway, $\frac{1}{2}$ mile north of Ferryhill Station.

Old Quarrington: Quarry $\frac{1}{4}$ mile east of Old Quarrington, 4 miles south-east of Durham.

Castleton Road End: 200 yards south of the Washington-Monkwearmouth road, 2 miles from Monkwearmouth.

Hylton West Town Moor: Quarry on north side of Washington-Monkwearmouth road, 3 miles from Monkwearmouth.

Carr Hill: 500 yards south of Flinton Hill Farm, 3 miles from Sunderland on the Sunderland/Chester-le-Street road.

Pontefract: (Commercial sample).

Harthill: Quarry 1 mile south of Harthill, 10 miles south-east of Sheffield.

II.—PETROLOGY.

Constituent Minerals.

Quartz, quartzite and felspar are the most important constituents of the sands. The minor constituents include limonite, a clay mineral which may be kaolin, and heavy minerals such as garnet, rutile, tourmaline and zircon. Muscovite mica is present at some localities.

The quartz grains are of two sizes; the larger ones are 0.50 mm. or more in dia., while the smaller ones vary from 0.15 mm. to 0.05 mm. across. Fig. 66 shows the large and small grains in the sand from the bottom bed of Crime Rigg Quarry. The grains are partly coated with limonite and clay minerals. The large grains are well rounded, while the small ones are subangular. The large clean grains have a finely frosted appearance due to wind abrasion, but the small grains are abraded only on the corners; this grain abrasion is important, for when a bond is added to the sand, the bond makes strong junctions with the grains. In some of the quartz grains inclusions are arranged linearly, while in others they are scattered irregularly.

Grains of quartzite are nearly as frequent as those of quartz at some localities, and differ from those of quartz only in their internal structure. They are composed of quartz granules closely sutured together and having random orientation. Two quartzite grains are shown in Fig. 67. On heating, internal stresses may be set up in the composite grains, which may shatter them. Such shattering is only likely to occur at the temperatures attained by sand in contact with molten iron or steel, and may have some slight effect on the surface of the casting.

Felspar grains are not numerous, and, in the samples examined, never exceed 5% of the sand. Microcline is the most important felspar present and is slightly sericitised. Versey considered that "the large amount of kaolin at Garforth and Harthill points to the decay of much feldspathic material. At the latter place kaolin is very abundant in the interstices between the grains." The presence of kaolin or a related clay mineral increases the strength of a sand for moulding purposes. The limonite attached to the surface of the quartz grains is a valuable bond. Its distribution is irregular, some of the grains being well-coated, while others are almost clean. Light milling of the sand distributes the limonite more evenly.

Grading.

The sieve analyses of the Permian Sands are given in Tables XXXIII. and XXXIV.

TABLE XXXIII.—*Mechanical Gradings of the Sands.*

Locality.	Percentage on B.S.I. Sieve No.—										Total. %.
	10.	16.	22.	30.	44.	60.	72.	100.	150.	Thro' 150.	
Sherburn Hill.	5.94	0.48	2.21	9.48	24.39	17.38	15.26	22.73	4.45	2.02	99.34
Hetton Downs	1.62	0.93	1.16	5.05	17.21	12.61	20.62	26.41	11.31	2.77	99.69
Coxhoe . .	1.17	2.21	8.98	9.39	13.71	17.68	2.59	24.12	13.23	6.35	99.43
Downhill	3.94	1.98	5.23	11.74	14.46	17.45	3.09	18.92	18.11	5.08	100.00
Crime Rigg :											
Top . .	0.00	0.68	3.91	12.24	26.68	13.61	12.91	20.53	7.41	2.25	100.22
Bottom . .	0.11	2.91	12.34	12.11	8.91	7.27	...	11.16	23.40	21.55	99.76
Ferryhill	3.91	10.66	5.12	2.70	2.33	3.30	2.43	28.63	33.84	6.66	99.58
Old Quarring-											
ton . .	1.37	0.55	2.87	5.24	21.48	30.36	...	24.33	9.94	3.64	99.78
Castleton											
Road End .	0.00	0.05	0.71	0.97	2.81	5.78	17.43	37.82	28.62	5.64	99.83
Hylton West											
Town Moor.	0.00	0.98	11.03	22.90	14.09	8.38	6.10	12.55	14.88	8.54	99.45
Carr Hill . .	0.00	0.11	2.31	6.78	19.10	22.50	20.90	18.10	7.40	2.81	100.01
Pontefract .	0.30	0.33	1.10	1.46	3.62	9.22	9.16	49.57	21.23	3.90	99.89
Harthill :											
Top . .	1.63	1.92	2.50	4.21	12.46	21.73	...	34.12	15.14	5.92	99.63
Bottom . .	0.19	1.87	3.82	5.11	10.54	23.83	...	39.76	9.02	5.86	100.00

Typical cumulative grading curves are shown in Fig. 70. They are of two forms : The curves for the sands from Pontefract and Harthill (the unnamed curve in Fig. 70) rise sharply between the ordinates corresponding to grains between 0.25 mm. and 0.15 mm. in dia.; the sand from Castleton Road End has a similar grading. The uniform grain size of these sands is illustrated by Figs. 68 and 69. The second form of grading curve is stepped, and is illustrated by the curve for Hylton West Town Moor, Fig. 70. The steep portion of this curve to the left of the 0.35-mm. ordinate indicates the grading of the large grains, while the steep portion to the right of the 0.25-mm. ordinate indicates the grading of the small grains. A similar "stepped" curve is shown for the sand from Hetton Downs. The width of the step

TABLE XXXIV.—*Cumulative Gradings of the Sands.*

Locality.	Percentage on B.S.I. Sieve No.—								
	10.	16.	22.	30.	44.	60.	72.	100.	150.
Sherburn Hill	0.94	1.42	3.63	13.11	37.50	54.88	70.14	92.87	97.82
Hetton Downs	1.62	2.55	3.71	8.70	25.97	38.58	59.20	85.61	96.92
Coxhoe	1.17	3.38	12.36	21.75	35.46	53.14	55.73	79.85	93.08
Downhill	3.94	5.92	11.15	22.89	37.35	54.80	57.89	76.81	94.92
Crime Rigg : Top	0.00	0.68	4.59	16.83	43.51	57.12	70.03	90.56	97.97
Bottom	0.11	3.02	15.36	27.47	36.38	43.65	...	54.81	78.21
Ferryhill	3.91	14.57	19.69	22.39	24.72	28.02	30.45	59.08	92.92
Old Quarrington	1.37	1.92	4.79	10.03	31.51	61.87	...	86.20	96.14
Castleton Road End	0.00	0.05	0.76	1.73	4.54	10.32	27.75	65.57	94.19
Hylton West Town Moor	0.00	0.98	12.01	34.91	49.00	57.38	63.48	76.03	90.91
Carr Hill	0.00	0.11	2.42	9.20	28.30	50.80	71.70	89.80	97.20
Pontefract	0.30	0.63	1.73	3.19	6.81	16.03	25.19	74.76	95.99
Harthill : Top	0.19	2.06	5.88	10.99	21.53	45.36	...	85.12	94.14
Bottom	1.63	3.55	6.05	10.26	22.72	44.45	...	78.57	93.71

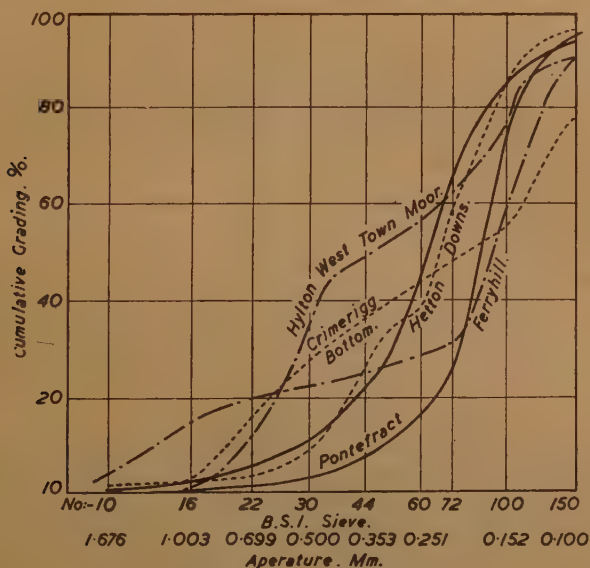


FIG. 70.—Grading Curves.

is a measure of the difference in grain size between the two grades; the sands from Hetton Downs and Hylton West Town Moor have only a small gap between the two grades, while those from Crime Rigg Bottom and Ferryhill have a wide gap between the two grades.

III.—CHEMICAL COMPOSITION.

Analyses of typical Permian Sands are given in Table XXXV. The proportion of silica ranges from 85% to 94%. A small

amount of titania is present, mostly as leucoxene. The iron content is low, 1% or less, and is due to the presence of limonite. The proportion of alumina varies from 1% to 6%, that is, some of the sands, notably Pontefract and Crime Rigg Bottom, contain a fair proportion of clayey minerals; the felspar content of the sands would account for only a small part of the alumina. The lime content varies from 0.20% to 2.5%, and depends on the leaching to which the sand has been subject. The magnesia content is similar to the lime content, except in the case of Downhill, which is particularly low. The alkalis were calculated as potash; though high for a refractory sand, they are not too high for steel-moulding work.

TABLE XXXV.—*The Chemical Compositions of Typical Permian Sands.**

	Pontefract.	Carr Hill.	Hylton West Town Moor.	Harthill Bottom.	Crime Rigg Bottom.	Downhill.
SiO ₂ . % .	85.20	93.25	91.00	89.30	91.34	86.70
TiO ₂ . % .	0.19	0.13	0.16	0.20	0.30	0.13
FeO. % .	0.96	0.59	0.51	4.81	1.08	1.20
Al ₂ O ₃ . % .	5.95	3.88	4.23	1.19	5.47	3.82
CaO. % .	1.90	0.20	0.70	0.60	0.20	2.45
MgO. % .	1.08	0.13	0.65	0.60	0.07	0.43
K ₂ O. % .	1.24	1.24	0.54	1.42	0.24	1.56
Loss. % .	3.00	0.50	1.80	1.75	1.00	3.20
Total. % .	99.52	99.92	99.59	99.87	99.70	99.49

* Analyses by N. E. Dobbins, Ph.D., M.Sc., Refractories Department, Sheffield University.

IV.—MOULDING PROPERTIES.

The tests of the moulding properties were made on standard A.F.A. test-pieces rammed either three or ten times. The dry-strength tests were made after the test-pieces had been dried at 200° C. for 2 hr. and allowed to cool to room temperature.

The Permian Sands have but little natural bond, and only the samples rich in silt have an appreciable green strength. For instance, the sand from the bottom bed of Crime Rigg Quarry gave the following results when tested without the addition of bond :

	3 Rams.	10 Rams.
Green strength . . .	5.41 lb. per sq. in.	9.25 lb. per sq. in.
Permeability number . .	29	21

When dried, the test-pieces were too friable to handle. The above figures are typical of "sands" containing a large proportion of silt and little clay.

The strength of the sands was improved by the addition of 5%

of ball clay. The comparative strengths and permeability numbers of the bonded sands are given in Table XXXVI.

TABLE XXXVI.—*The Moulding Properties of the Permian Sands.*

	Moisture. %.	No. of Rams.	Weight of Test-Piece. G.	Green Strength. Lb. per sq. in.	Permea- bility No.	Dry Strength. Lb. per sq. in.
Hetton Downs*	3	3	170	7.8	89	10.8
	3	10	178	13.0	61	
Coxhoe	3	3	173	8.9	54	9.5
	3	10	178	13.5	38	
Downhill	4	3	173	11.7	54	11.9
	4	10	178	16.2	32	
Crime Rigg	4	3	172	9.6	84	7.0
Top *	4	10	180	12.4	60	
Crime Rigg	3	3	176	12.6	21	17.2
Bottom	3	10	180	15.7	14	
Ferryhill	5	3	168	9.2	32	23.0
	5	10	174	15.1	22	
Castleton Road	3	3	165	9.1	45	19.5
End	3	10	167	13.1	34	
Hylton West	3	3	172	11.6	46	23.8
Town Moor	3	10	180	16.7	23	
Carr Hill	4	3	170	4.4	111	11.8
	4	10	173	6.8	95	
Pontefract	4	3	170	12.1	32	11.1
	4	10	178	10.5	21	
Harthill Top	4	3	173	8.5	31	6.4
	4	10	178	15.1	23	
Harthill	3	3	173	8.3	37	8.9
Bottom	3	10	178	11.3	30	

* Bonded with 7.5% of ball clay.

Green Strength.

The green strength of the sands when bonded with 5% of ball clay ranges from 8 to 12 lb. per sq. in. (for test-pieces rammed three times), with the exception of Carr Hill.

The sands from Downhill, the bottom bed of Crime Rigg Quarry and Hylton West Town Moor have high green strengths and show marked double grading with a high proportion of large grains.

The sand from Coxhoe has a grading similar to that of the sand from Downhill, but it contains less clay than the latter and consequently its green strength is lower. The sand from Ferryhill has more marked double grading, but contains less clay than that from Downhill and consequently has a lower green strength.

The sands from Castleton Road End, Harthill and Pontefract are single-graded. The first two have low green strengths, about 8 lb. per sq. in. That from Pontefract is stronger, because it contains more clay and is finer-grained.

Permeability.

In general, fine-grained sands have a lower permeability number than coarse-grained sands. This statement must be modified when applied to double-graded sands, for it can be shown that close packing may be obtained with a mixture of 50% fine grains.

The sands with comparatively high green strengths have low permeability numbers and *vice-versa*, that is, high green strength is obtained when the sand packs closely.

The sands with permeability numbers below 50 are not so permeable as most of the sands in use in steel foundries. The permeability of the sands could be improved either by washing out some of the silt or by blending with a coarser sand.

Dry Strength.

The dry strengths of the sands are low compared with the dry-sand mixes used in steel foundries. The sands with high green strengths have high dry strengths and *vice-versa*.

Refractoriness.

The Permian Sands were not recommended by Boswell, on account of their high lime content. Though some of the sands, such as those from Pontefract and Downhill, have a high lime content and low refractoriness, others have a low lime content and are sufficiently refractory for steel-moulding work.

Standard A.F.A. test-pieces of the sands bonded with 5% of ball clay (two with 7.5%) were fired at 1550° C. for 2 hr.; the results are summarised in Table XXXVII.

TABLE XXXVII.—*The Refractoriness of the Permian Sands.*

Bonded with 5% of ball clay, except those marked; fired at 1550° C. for 2 hr.

Locality.	Shrinkage. %.	Remarks.
Hetton Downs * . . .	12.5	Slightly glazed; open texture.
Coxhoe	Squatted; well glazed.
Downhill	Fused completely.
Crime Rigg: Top * . .	10	Slightly glazed; open texture.
Bottom . .	15	Well glazed; close texture.
Ferryhill	Fused completely.
Castleton Road End . .	12.5	Slightly glazed; slightly cracked; open texture.
Hylton West Town Moor	12.5	Glazed; slightly cracked; fairly open texture.
Carr Hill	5	Slightly glazed; slightly cracked; open texture.
Pontefract	Almost fused.
Harthill: Bottom	Almost fused.
Top	Fused completely.

* Bonded with 7.5% of ball clay.

The sands for which shrinkage percentages are given are as refractory as many sands used for steel-moulding purposes. The remaining sands might be suitable for iron-moulding, but are not refractory enough for steel-moulding.

V.—CONCLUSION.

When bonded artificially, the sands from Hetton Downs, Crime Rigg, Castleton Road End, Hylton West Town Moor and Carr Hill have moulding properties approaching those of sand mixtures in use in steel foundries. It is probable that their moulding properties could be improved, by the addition of extra bond and by washing to remove some of the silt, so that they could be used in steel foundries.



THE MAINTENANCE OF THE FURNACE LININGS IN LARGE BASIC OPEN-HEARTH TILTING FURNACES BY THE USE OF CHROME ORE, MAGNESITE AND SERPENTINE.

BY A. JACKSON (APPLEBY-FRODINGHAM STEEL CO., LTD., SCUNTHORPE).

SUMMARY.

In a recent paper, "The Linings of Large Basic Open-Hearth Tilting Furnaces" (*Journal of The Iron and Steel Institute*, 1942, No. II., pp. 9 P-16 P), developments in economising in the use of magnesite bricks for large open-hearth tilting furnaces were described. This included discussion of the usefulness of stabilised dolomite bricks, the importance of the quality of "Basic" and reduction in the number of chrome-magnesite bricks used in front walls.

The information then given is now supplemented by a discussion of the use of parging pastes containing chrome ore and serpentine, with the object of reducing still further the consumption of magnesite. The possibility of reducing the consumption of chrome ore is also considered. Results obtained with various mixtures of magnesite, chrome ore and serpentine are described.

APPLEBY-FRODINGHAM steel furnaces have always used more chrome ore and magnesite as paste for lining repairs than chrome-magnesite and magnesite as bricks. Before 1939 the materials used for making this paste were relatively cheap and their use was therefore economic.

Since 1939 considerable efforts have been made, first to reduce the magnesite consumption, even at the expense of increasing the chrome ore, later to reduce the chrome ore as well as magnesite consumed and finally to replace both of these materials to the greatest possible extent by substitutes.

TABLE I.—*Annual Consumption of Chrome Ore, Magnesite and Serpentine.*

Period.	Consumption, lb. per ton of Ingots, of—		
	Chrome Ore.	Magnesite, &c.	Serpentine.
1936-1939	5.90	6.25	Nil
Year ending June 1940	10.45	5.28	Nil
1941	8.80	4.58	Nil
1942	7.04	4.06	Nil
1943	2.09	2.84	3.45

Table I. shows the annual consumption of chrome ore, magnesite and serpentine per ton of production over the last four years, compared with pre-war averages for the 250- and 300-ton furnaces at the Appleby melting shop.

The figures for "magnesite, &c." consist of magnesite and chrome-magnesite brick end recoveries (comprising some 50% of all bricks used) and double-burned magnesite peas. Only a small proportion of the above materials is used on portions of the furnace other than the front lining.

The points affecting the changes in consumption are as follows :

- (1) The percentage of chrome ore in the paste was increased considerably and some magnesite saving resulted.

- (2) The chrome ore percentage was steadily reduced to give a minimum total consumption of chrome ore plus magnesite.

- (3) The front bank was fettled after the whole of the scrap, &c., was charged, but before the addition of the hot metal. This enabled pasting to commence at a slightly higher level, but used more dolomite.

- (4) Stable dolomite cement was used in place of magnesite powder for rebuilds.

- (5) Water-cooling of the front lining was used earlier, but was abandoned towards the end of 1942.

- (6) More basic bricks were used in the splays and less patching paste was therefore necessary.

These points were responsible for the alteration up to about the end of 1942.

Serpentine.

Concerning the use of serpentine, laboratory trials, commenced in June, 1942, showed that an 80/20 mixture of serpentine-magnesite (the magnesite being largely in the fine fraction) best satisfied the combined requirements of refractoriness and economy of chrome ore and magnesite. Subsequent practical trials confirmed this view. Mixtures of chrome ore and serpentine were definitely less good and were considered unsatisfactory for this purpose.

This new paste was again a stage less good than the material that it replaced. In consequence, as the front of the furnace was continuous steel plate, shut-downs for repairs became more frequent.

To overcome this trouble, the structural work of the furnace front was strengthened and openings were cut through the plate-work between each door, which could be covered during operations by a detachable steel plate wedged into position. By this means some new brickwork could be put into the lining without taking the furnace off. It was only with reluctance that the continuous steel-cased front was abandoned, but only the possibility of putting

in new brickwork by this means, coupled with the fact that the doors on Appleby furnaces are relatively close together and have narrow jambs, easily accessible for pasting, enabled this serpentine material to be used. Some extra chrome-magnesite brick is now used, but this is much less than the saving in chrome ore and magnesite resulting from the various alterations.

The older tilting furnaces of smaller capacity at the Frodingham melting shop have only three doors and consequently very wide jambs. Furthermore, the design of the furnace front will not permit of alteration on the above lines; we have, therefore, not as yet been able to adapt, with any degree of satisfaction, the less good type of paste to this plant.

The following is the grading of the 80/20 serpentine-magnesite paste :

Moisture content 22·8%.

Grading on British Standard sieves :

On 7 mesh	.	.	.	:	1·0%
„ 7-25 mesh	27·0%
„ 25-72 mesh	29·0%
„ 72-150 mesh	12·5%
Thro' 150 mesh	30·5%
					<hr/>
					100·0 %
					<hr/>

SOME TENSILE SHOCK PROPERTIES OF CARBON STEELS.*

By F. V. WARNOCK, M.Sc., Ph.D., F.R.C.Sc.I., M.I.MECH.E., AND
J. B. BRENNAN, M.Sc., Ph.D. (COLLEGE OF TECHNOLOGY, BELFAST).

SYNOPSIS.

Previous work carried out by Smith and Warnock on the tensile shock properties of Lowmoor iron formed the basis of a similar investigation embracing a family of carbon steels and carried out on the same testing machine. The residual energy after fracture was accurately measured by a device designed for that purpose.

The results of static, single-shock and multi-shock tests are compared and show that both the single-shock energy and the ratio of the static energy to the single-shock energy are dependent on the carbon content. The elongation produced by single-shock tests differs in many cases from that obtained by static methods, but the reduction of area remains substantially unaffected by the method of testing. A limiting range of shock energy, dependent on the carbon content, was indicated. Maximum values of elongation and reduction of area were observed in the multi-shock tests. An increase in the number of shocks for rupture caused a rapid diminution in the values of these quantities.

Introduction.

THE behaviour of engineering materials under shock loads has been the subject of many investigations. Disagreement abounds amongst the results of these investigations, chiefly because it was, and is, expedient to measure shock or impact in terms of the energy of the shock-producing hammer or tup, and little attempt was made to account for all the energy available. When such an attempt was made the devices employed were only partially successful, owing either to their delicate and elaborate nature or to the severity of the loading imposed upon them.

A machine designed by one of the authors of the present paper has been described in a previous *Journal* of the Institute,⁽¹⁾ together with a preliminary investigation of the behaviour of Lowmoor iron when subjected to both single- and multiple-shock tests. This machine, a simple mechanical device in which elaborate measuring apparatus is eliminated, enables valuable information to be obtained from tests of this nature.

In the multi-shock tests a small amount of residual energy was unaccounted for, and the authors have devised a method whereby the actual energy absorbed by the specimen during such tests can be calculated.

It was suggested that the behaviour of a pure iron under such loading might be different from that of a carbon steel, and the present paper is the result of similar investigations on a family of

* Received February 13, 1943.

carbon steels, in which the above machine, together with a simple additional measuring device, has been used.

Briefly the construction and operation of the machine is as follows.

The Testing Machine.

Fig. 1 is a diagrammatic representation of the machine. A rotating crank *C*, of variable throw, is attached to a wheel *B* through an adjustable turnbuckle *L* by means of a wire rope. Another wheel *W*, keyed to the same shaft as *B*, is attached in a similar way to the mass *X*, which is connected through an automatic gripping and releasing device to the arresting crosshead *M*. The specimen *S* is attached at one end to the arresting crosshead and at the other end to the tup *T*. Rotation of crank *C* causes *M*, *S* and *T* to become attached to *X* and then lifted vertically. At any predetermined height *M*, *S* and *T*, released automatically, fall freely on to the anvil *R*, contact being made through suitable striking surfaces on *M* and *R*. The specimen is then subjected to a momentary tensile stress due to sudden retardation of the tup. By driving the crank *C* from a suitable motor, this cycle of operations may be repeated until fracture of the specimen occurs. The driving gear used was of such a nature that 40 shocks per min. took place throughout the multi-shock tests.

FIG. 1.—Diagrammatic Representation of the Testing Machine.

Consideration of the type of loading employed led to the word "shock" being substituted for "impact," which implies collision between two bodies, one of which is the test-piece, and has been interpreted as such by many experimenters when investigating the effects of suddenly applied stress.

The Specimen.

The specimen previously used in the machine was screwed at each end with a $\frac{3}{4}$ -in. dia. Whitworth thread, and reduced to $\frac{1}{4}$ in. dia. at the centre for a gauge length of $\frac{3}{4}$ in. The reduction was by means of fillets of $\frac{3}{8}$ -in. radius. One end of the specimen was screwed into the arresting crosshead of the machine and the other

end into the tup. Each end was locked in position by means of a nut and spring washer. This method of preventing the specimen from working loose under repeated shock was found to be extremely satisfactory.

For various reasons, of which not the least was the cost of manufacture, a new form of specimen had to be adopted for this investigation, and difficulty was experienced in designing a specimen to which a simple and effective gripping device could be applied. The severe action of shock loads on a taper form of grip is clearly indicated in the following description of tests carried out on the machine. These tests were undertaken in an endeavour to obtain a satisfactory device which might be used to hold the specimen firmly in position throughout a test consisting of many shocks.

Since re-design was necessary, it was decided so to fashion the specimen that it could be used equally well in a static tensile testing machine, an alternating direct-stress testing machine (which were available) and the repeated-shock machine. The specimen used in the fatigue machine had tapered ends and was reduced at the centre in a similar way to the screwed specimen of the shock machine. Special split chucks were made, tapered on the inside and screwed on the outside, to adapt the fatigue specimen for use in the shock machine. These chucks were of robust construction. One complete chuck with a tapered end of a fatigue specimen inside was screwed into a hole, tapped in the tup, and locked in position by means of a spring washer, the second chuck, containing the other end of the specimen, being screwed into the arresting crosshead and locked in a similar manner. To test the chucks for creep under load, the specimen was not reduced at the centre, to eliminate plastic extension.

The machine was set to give quite a normal height of fall, namely 4 ft. The distance between the face of the tup and the face of the arresting crosshead was measured by means of a micrometer. After each of 10 successive shocks, this distance was found to have increased by increments of approximately 0.025 in. On inspection after removal from the machine it was found that there had been no appreciable creep or distortion of the threads of the chuck or of the specimen itself. Relative movement, however, had taken place between the surfaces of the tapered ends of the specimen and the tapered surfaces of the chucks. Originally smooth and well finished, these surfaces were now quite rough and literally torn up. It was thought that parting of the half chucks had been responsible for the damage to the tapered surfaces, and a new arrangement was designed.

The specimen was tapered at each end, the taper being 1 in 8 as before, but one end was smaller in diameter than the other. The tup was made hollow, and the small end of the specimen, passing right up through it, was locked in the arresting crosshead by means of taper collets made from cast iron.

A similar test was applied and similar creeps were observed. The top end of the specimen suffered more severely, as in the previous test, though there was little evidence of surface deformation of the cast-iron collets. The weight of tup used in each test was 7 lb.

It was then evident that the idea of using a taper gripping device had to be discarded. Accordingly, another specimen was designed, the dimensions of which are given in Fig. 2. Care was



FIG. 2.—The Specimen.

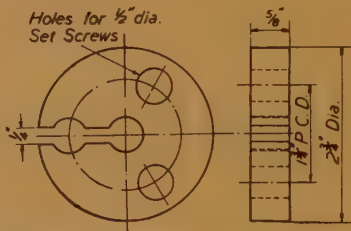


FIG. 3.—Locking Plate for the Specimen.

taken to provide as large a bearing surface as possible on the face of each of the collars shown in Fig. 2, to avoid distortion under load. At the same time the diameter of the parallel portions between the gauge length and the collars had to be of such a dimension that permanent extension would not take place. The specimen was secured in position at each end by means of locking plates, each locking plate being drilled and slotted as in Fig. 3.

To fasten the specimen in the machine, the $\frac{1}{4}$ -in. dia. portion was passed through the slot in each locking plate in turn, the locking plates being then pushed up against their respective collars. One end of the specimen was inserted in a hole in the top of the 7-lb. tup, the depth of the hole being such that when the specimen was pushed home the surface of the collar was $\frac{1}{64}$ in. above the surface of the tup. The set-screws used to hold the locking plates in position were prevented from working loose by means of spring washers. A similar procedure was carried out to fasten the other end of the specimen to the arresting crosshead. Fig. 4 shows the specimen attached to the tup and to the arresting crosshead. The method of securing and the specimen itself gave complete satisfaction throughout the tests described in this paper. The specimen was adaptable for use in either the alternating-stress fatigue testing machine or the static tensile testing machine.

The Measurement of Residual Energy.

When a specimen is fractured in an impact machine, only part of the energy imparted to the pendulum or tup is used to rupture the test-piece. The remaining energy is called the residual energy.

As already stated, there was no method available for the measurement of this quantity in the previous investigations.⁽¹⁾ As the number of blows increases the percentage error in neglecting the residual energy of the tup in the last shock decreases. Accordingly Smith and Warnock⁽¹⁾ plotted $\log N$ against $\log H$, where N represents the number of shocks to fracture and H the height fallen by the tup. This graph was a straight line. It was an easy matter to extend the curve backwards to cut the N axis and thus obtain the value of the energy required for rupture by a single shock. If, however, a residual-energy dynamometer were available, the

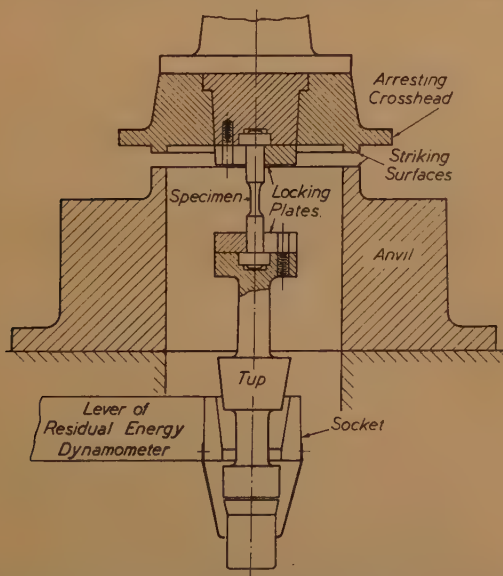


FIG. 4.—Section through the Arresting Crosshead and Anvil, showing the specimen and tup in position.

amount of work and the number of specimens required to determine the value of the single-shock energy would be greatly reduced.

Several forms of residual-energy measurement used by previous investigators were considered, and each rejected in turn because of some quality incompatible with the requirements and limits of the machine in use. The following was decided on, and gave satisfactory service.

The tup, after fracture of the specimen, fell into a socket in one end of a simple lever at rest. The lever was balanced with the tup in the socket, and, on receiving the falling tup, proceeded to rotate about the centre of gravity of the lever and tup, in a vertical plane. This rotation was opposed by a helical spring, the

energy of rotation of the lever and tup being converted into strain energy of the spring. Now, in an arrangement of this nature, the kinetic energy of rotation of the lever on receiving the falling tup is a definite fraction of the kinetic energy of the tup just before entering the socket, assuming that the tup does not rebound from the socket but moves as one with the lever. This is provided for by using a taper socket and spring clips which hold the tup firmly in position. Since the strain energy of the spring is proportional to the square of the extension of the spring, the kinetic energy of

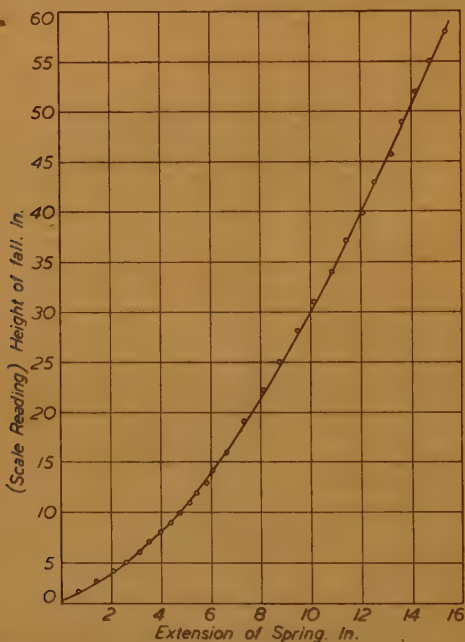


FIG. 5.—Measurement of Residual Energy in the Tup. Calibration curve connecting the height of fall of the tup and the extension of the spring.

the tup before entering the socket is proportional to the square of the extension of the spring. The kinetic energy of the tup is composed of the residual energy after fracture and a small constant value due to a fixed height of fall of the tup between fracture and entering the socket. Accordingly the residual energy of the tup and the extension of the spring should have a parabolic relationship. Fig. 5 shows a calibration curve connecting the height of fall of the tup and the extension of the spring.

The principal dimensions of the residual-energy dynamometer are given in Fig. 6. The lever was attached to a shaft which rotated in two self-aligning ball bearings. One half of the lever,

keyed to the shaft between the bearings, contained the tapered socket. The other half, composed of flat bars attached to the extremities of the shaft, carried balance weights. A circular scale was fixed at one end of the apparatus and a pointer was screwed to one end of the shaft. The pointer, rotating with the lever, moved over the scale to give a reading of the maximum deflection. The inertia of the rotating system was such that the lever rotated

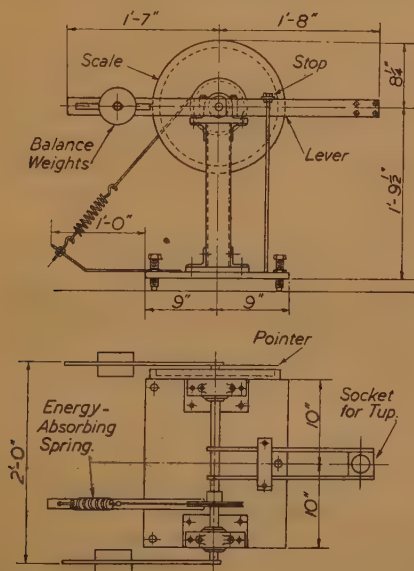


FIG. 6.—The Residual-Energy Dynamometer.

slowly until brought to rest by the spring, and then returned slowly to the initial position. Two stops were provided, one to retain the lever in a horizontal position and one to prevent over-strain of the spring. The maximum possible deflection of the lever was 270° .

For calibration purposes the apparatus was placed in the correct working position, the longitudinal axis of the socket coinciding with the vertical centre-line of the machine, and directly below the anvil as in Fig. 4. The tup containing a half specimen was dropped from a series of heights and the corresponding deflection of the pointer marked on the scale. The tup was released by ignition of a thread by which it was attached to the raised arresting crosshead. The maximum residual energy which the apparatus was capable of absorbing was 400 in.lb. The necessity for this high figure arose from a consideration of the possible residual energy in a test consisting of a small number of shocks. Each

scale reading was checked several times, and it was estimated that the maximum error was approximately 1.2% of the total energy of rupture for any test of which the machine was capable.

To obtain the value of the energy required to rupture a specimen by a single shock, the machine was adjusted so that the releasing triggers came into action when the tup was at a height equivalent to the value of the energy required to rupture the specimen by static means. Sudden arrest of the tup by the anvil, through the specimen, caused rupture of the specimen. The tup then fell freely into the socket attached to the residual-energy dynamometer, the angle of rotation of the beam of the dynamometer being read as height of fall of the tup and called the "residual height."

Let W be the weight of the tup, H the height of fall of the tup, h the residual height, and K the height of fall of the tup from the position of impact to the position of zero reading in the residual-energy apparatus. Then :

$$\text{The energy required to rupture the specimen} = W(H + K - h).$$

The value of K used throughout the tests was $\frac{3}{4}$ in.

Again, let N be the number of shocks during the last of which the specimen ruptured. Then :

$$\text{The actual number of shocks to cause rupture} = N - \frac{h - K}{H}.$$

The Tup.

Examination of the results obtained by Smith and Warnock ⁽¹⁾ showed that the energy required to rupture a $\frac{1}{4}$ -in. dia. specimen of Lowmoor iron was approximately 400 in.lb. The maximum height at which the machine could be operated was approximately 100 in. for single-shock tests. It was estimated that a 7-lb. tup, representing a maximum available amount of energy of 700 in.lb., would permit the machine to be used to the best advantage. Inspection of the results obtained (Tables II. to XII.) shows that the maximum single-shock energy for the steels tested was 600 in.lb.

The tup was turned from a length of $2\frac{3}{4}$ -in. mild-steel bar. It was necessary for the purposes of balancing that, when in position in the socket of the lever, the centre of gravity of the tup should coincide with the longitudinal centre-line of the lever. This, together with other factors, resulted in the form of tup shown in Fig. 4. The weight of the tup together with a half specimen, a locking plate, three set-screws and three spring washers was 7 lb.

Material used in the Investigation.

The material used in the tests recorded in this paper consisted of a family of steels of varying carbon content, the other constituents being approximately constant. The ten steels of the family were manufactured by the Steel Company of Scotland, Ltd., and supplied some years previously for stress endurance tests.

The steels were supplied in the form of 1-in. dia. bars, from which the specimens were machined. The material did not receive any heat treatment after manufacture.

The chemical analyses of the steels as supplied by the manufacturers, together with the results of tensile tests, are given in Table I. The tensile tests were carried out on a Riehle screw-testing machine, the specimens being 0.625 in. in dia. with enlarged ends.

TABLE I.—*Analyses and Tensile Properties of the Steels Investigated.*

Reference Letter :	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.
Carbon. % . . .	0.12	0.18	0.28	0.29	0.33	0.37	0.47	0.52	0.58	0.63
Silicon. % . . .	0.037	0.066	0.066	0.177	0.066	0.093	0.13	0.103	0.137	0.168
Sulphur. % . . .	0.03	0.04	0.035	0.03	0.035	0.033	0.031	0.042	0.028	0.035
Phosphorus. % . . .	0.02	0.04	0.037	0.011	0.032	0.024	0.045	0.032	0.029	0.032
Manganese. % . . .	0.56	0.56	0.78	0.62	0.66	0.65	0.6	0.72	0.63	0.53
Yield stress. Tons per sq. in.	17.0	17.5	20.5	19.6	19.9	21.4	21.8	23.9	26.2	...
Ultimate stress. Tons per sq. in.	24.2	26.9	33.4	34.8	34.2	38.3	41.2	44.4	50.7	52.3
Elongation on 4 in. length. %	35.0	35.0	25.5	25	27.3	24.3	23.5	20.8	16.3	13.3
Reduction of area. %	66.8	62.6	55.9	53.2	56.3	50.5	47.1	43.0	33.3	28
Brinell number	116	121	153	158	156	163	179	202	207	228

The Brinell hardness tests were carried out, using a 10-mm. ball and a load of 3,000 kg. for 15 sec., on short lengths cut from the bars. Two indents were made in the direction of the axis of the bar, and the average value was taken in each case.

Single-Shock Tests.

As shown in Tables II. to XI., several single-shock tests were carried out for each steel. The 0.12% carbon steel was the first

TABLE II.—*0.12% Carbon Steel.*

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on 1-in. Length. In.	Initial Diameter. In.	Final Diameter. In.	Reduction of Area. %.
1	81	5.5	534	1	534	0.2515	0.2505	0.142	67.8
2	78	0.5	548	1	548	0.25	0.25	0.141	68.2
3	78	3	530	1	530	0.244	0.25	0.142	67.7
4	78	1	544	1	544	0.235	0.25	0.142	67.7
5	78	2.5	534	1	534	0.236	0.25	0.142	67.7
6	66.5	53	466	1.2	559	0.251	0.25	0.14	68.6
7	54	31	378	1.44	546	0.234	0.251	0.14	68.9
8	42	37	294	2.14	627	0.274	0.25	0.14	68.6
9	30	4.3	210	2.89	608	0.278	0.25	0.142	67.7
10	19	14	132	6.29	698	0.279	0.2505	0.141	68.3
11	10	1.5	70	12.9	904	0.316	0.251	0.135	71
12	6	3	42	27.5	1,155	0.345	0.25	0.132	73
13	3	...	21	94	1,975	0.362	0.2505	0.124	76.1
14	2	...	14	147	2,058	0.34	0.25	0.129	73.3
15	0.87	...	6.09	579	4,026	0.385	0.25	0.124	75.2
16	0.72	...	5.04	10,002	50,410	0.385	0.2505	0.125	75.2
17	0.61	...	4.27	2,169	9,242	0.305	0.25	0.132	71.9

TABLE III.—0.18% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{2}$ -in. Length. In.	Initial Diameter. In.	Final Diameter. In.	Reduction of Area. %.
1	78	3.5	528	1	528	0.24	0.2505	0.142	67.9
2	78	3.25	529	1	529	0.23	0.2505	0.145	66.5
3	78	3	530	1	530	0.234	0.2505	0.144	66.9
4	48	18	336	1.64	551	0.231	0.2495	0.146	66.6
5	29	27	203	3.07	624	0.251	0.2505	0.149	64.6
6	20	9	14	4.58	641	0.276	0.25	0.141	68.2
7	14	6	98	7.61	745	0.278	0.2505	0.14	68.7
8	9	1	63	18.94	878	0.286	0.251	0.14	68.9
9	6	0.5	42	24	1,008	0.297	0.2505	0.142	67.9
10	4	3.5	28	32.2	901	0.317	0.251	0.139	79.4
11	2	...	14	168	2,212	0.327	0.2505	0.13	72.9
12	0.87	...	6.09	1,037	6,515	0.299	0.25	0.132	72
13	0.78	...	5.46	3,203	17,488	0.34	0.2505	0.133	71.8
14	0.72	...	5.04	4,593	23,049	0.288	0.25	0.135	70.6
15	0.675	...	4.73	15,583	73,708	0.15	0.25	0.225	18.9
16	0.61	...	4.27	37,167	158,703	0.233	0.25	0.17	53.9

TABLE IV.—0.28% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{2}$ -in. Length. In.	Initial Diameter. In.	Final Diameter. In.	Reduction of Area. %.
1	90	4	607	1	607	0.187	0.2505	0.17	55.6
2	90	4.75	602	1	602	0.185	0.26	0.172	54
3	90	6.5	585	1	585	0.182	0.25	0.172	53.8
4	48	8.75	336	1.83	615	0.19	0.25	0.176	51.9
5	29	11	203	3.65	740	0.201	0.25	0.172	50.4
6	20	1.6	140	5.95	833	0.213	0.25	0.168	51.9
7	14	6.75	98	10.55	1,030	0.214	0.2505	0.165	54.9
8	9	0.5	63	23.93	1,506	0.237	0.2505	0.162	56.7
9	6	2	42	35.75	1,502	0.226	0.2505	0.162	58.2
10	4	2.5	28	95	2,660	0.237	0.2505	0.161	58.8
11	2	...	14	1,287	18,020	0.205	0.2505	0.181	47.8

TABLE V.—0.29% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{2}$ -in. Length. In.	Initial Diameter. In.	Final Diameter. In.	Reduction of Area. %.
1	78	0.25	546	1	546	0.21	0.251	0.173	52.4
2	78	0.5	546	1	546	0.186	0.2505	0.175	52.6
3	78	0.625	546	1	546	0.196	0.2505	0.175	51.2
4	48	5.5	336	2.88	968	0.2	0.25	0.173	51
5	29	12.25	203	3.6	730	0.214	0.2505	0.168	52.2
6	20	2.25	140	4.91	688	0.227	0.2505	0.164	55.1
7	14	2.5	98	8.86	868	0.226	0.25	0.162	57
8	9	0.6	63	21	1,328	0.241	0.2495	0.167	57.3
9	6	2.5	42	26.66	1,120	0.235	0.249	0.166	55
10	4	3.5	28	76.25	2,135	0.272	0.2505	0.166	56.1
11	2	...	14	597	8,360	0.253	0.2505	0.168	55.3

TABLE VI.—0.33% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	84	2	579	1	579	0.202	0.251	0.164	56.2
2	84	3.6	568	1	568	0.2	0.25	0.167	55.4
3	84	2.5	576	1	576	0.21	0.2505	0.162	58.2
4	48	0.75	356	1.99	669	0.226	0.2505	0.166	56.1
5	29	0.25	203	3	609	0.211	0.25	0.165	56.5
6	20	9.25	140	5.56	779	0.235	0.25	0.163	57.4
7	14	0.6	98	9	882	0.234	0.2505	0.163	57.9
8	9	0.7	63	19	1,196	0.246	0.251	0.159	59.9
9	6	3	42	30.6	1,327	0.261	0.2505	0.154	62.2
10	4	1.25	28	65.9	1,946	0.284	0.2505	0.153	62.7
11	2	...	14	764	10,700	0.264	0.25	0.162	57.9

TABLE VII.—0.37% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	84	4.5	562	1	562	0.179	0.2505	0.175	51.2
2	84	5.5	555	1	555	0.176	0.2505	0.175	51.2
3	84	5.75	553	1	553	0.175	0.25	0.174	52.5
4	48	7.75	336	1.85	632	0.19	0.2505	0.176	50.6
5	29	14	203	3.54	718	0.191	0.2505	0.177	50.0
6	20	19	140	5.08	711	0.183	0.25	0.175	51.1
7	14	0.5	98	11	1,078	0.224	0.25	0.17	53.8
8	9	3	63	24.7	1,556	0.228	0.2505	0.17	54.0
9	6	1.5	42	36.8	1,545	0.23	0.2505	0.169	54.5
10	4	4	28	193	5,405	0.254	0.251	0.171	53.7
11	2	...	14	1,398	19,580	0.177	0.2505	0.196	38.9

TABLE VIII.—0.47% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	84	4.75	560	1	560	0.17	0.2505	0.18	48.4
2	84	2.5	576	1	576	0.163	0.2505	0.179	48.9
3	84	3.5	569	1	569	0.166	0.2505	0.178	49.5
4	48	4	336	1.93	648	0.183	0.2505	0.183	46.7
5	29	6.5	203	3.79	770	0.191	0.25	0.171	49.8
6	20	1.3	140	5.96	836	0.184	0.25	0.175	51
7	14	3	98	10.83	1,061	0.184	0.2495	0.18	47.9
8	9	0.5	63	23	1,765	0.211	0.2495	0.179	48.6
9	6	1	42	41.9	1,718	0.21	0.25	0.175	51
10	4	0.5	28	156	4,370	0.222	0.25	0.178	49.3
11	2	...	14	1,869	26,180	0.138	0.2505	0.207	31.85

TABLE IX.—0.52% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	90	12.5	548	1	548	0.155	0.25	0.186	44.6
2	90	9.75	567	1	567	0.156	0.2505	0.185	45.5
3	90	9.25	569	1	569	0.156	0.25	0.182	47.1
4	48	4.2	336	1.92	646	0.17	0.25	0.186	44.6
5	29	14	203	3.54	718	0.165	0.25	0.187	44
6	20	4.5	140	6.8	953	0.178	0.25	0.183	46.8
7	14	0.25	98	14	1,372	0.186	0.25	0.183	46.8
8	9	3	63	30.7	1,936	0.189	0.25	0.181	46.8
9	6	2.25	42	59.7	2,501	0.201	0.25	0.18	47.5
10	4	0.5	28	239	6,597	0.214	0.2505	0.192	41.3
11	2	...	14	3,181	43,880	0.065	0.2505	0.227	17.85

TABLE X.—0.58% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	84	7.75	539	1	539	0.121	0.2505	0.2	21.3
2	84	10.75	518	1	518	0.121	0.2505	0.2	21.3
3	84	12	509	1	509	0.116	0.2505	0.201	21.3
4	48	11	336	1.79	602	0.134	0.2505	0.203	16.04
5	29	11.5	203	3.63	737	0.119	0.2505	0.202	12.45
6	20	1.25	140	6.97	975	0.13	0.25	0.201	10.35
7	14	0.5	98	17	1,665	0.145	0.25	0.201	8.66
8	9	3.5	63	46.7	2,940	0.13	0.25	0.208	6.94
9	6	2.5	42	96.7	4,060	0.123	0.25	0.208	5.68
10	4	...	28	879	24,600	0.067	0.2505	0.225	4.63
11	2	...	14	3,074	43,080	0.022	0.2507	0.242	3.26

TABLE XI.—0.63% Carbon Steel.

Test No.	Height fallen. In.	Residual Height as read. In.	Energy per Shock. In.lb.	Number of Shocks.	Total Energy for Rupture. In.lb.	Extension on $\frac{1}{4}$ -in. Length. In.	Initial Di- ameter. In.	Final Di- ameter. In.	Reduction of Area. %.
1	84	10.5	520	1	520	0.122	0.2505	0.202	35.5
2	78	6	509	1	509	0.111	0.2505	0.206	32.6
3	78	4.25	522	1	522	0.113	0.2505	0.204	33.8
4	48	10.4	336	1.79	601	0.118	0.25	0.206	32
5	30	14	210	3.55	745	0.134	0.251	0.202	35.4
6	18.8	5	132	7.77	1,025	0.136	0.2505	0.203	34.4
7	12	0.25	84	18	1,511	0.135	0.2505	0.208	31.1
8	10	1.75	70	30.9	2,162	0.123	0.251	0.210	29.7
9	8	3	56	50	2,800	0.135	0.25	0.212	25.9
10	6	1	42	183	7,690	0.115	0.2505	0.217	24.9
11	3	...	21	1,438	29,500	0.146	0.25	0.24	7.4
12	2	...	14	3,621	60,694	0.025	0.2505	0.242	6.4

material to be tested, and five single-shock results were obtained. The scatter or maximum departure from the mean value was approximately 2%. The consistency of these results led to the

decision that three single-shock tests would be sufficient for each steel.

To compare the energy required for rupture by a single shock with the energy absorption by gradually applied stress, a specimen of each steel was ruptured in a Riehlé screw-testing machine. Each specimen was secured in the Riehlé machine by means of the locking plates designed for the shock machine. The locking plates were attached to self-centring chucks, suitable holes having been drilled and tapped in the ends of the chucks to receive the set-screws associated with the locking plates. The machine was operated by hand, observations being taken for load increments of 200 lb. The extensometer used read to 0.001 in. The load-extension curves were plotted to a large scale and the area under each was determined in order to obtain the energy required to fracture a specimen of each steel.

The average values of the single-shock energy and the corresponding values of the static energy are given in Table XII. The ratio of single-shock energy to static energy is almost unity for the steels with the least and greatest carbon content. These two results are in agreement with those obtained by Smith and Warrnock⁽¹⁾ for Lowmoor iron. It is significant, however, that the values of single-shock energy, including that obtained for Lowmoor iron, are less in each case than the corresponding static values—results which are at variance with those of other investigators, such as Blount, Kirkaldy and Sankey,⁽²⁾ Stanton and Bairstow,⁽³⁾ Wélikhow⁽⁴⁾ and Breuil.⁽⁵⁾

To check up possible sources of error, the Riehlé machine was calibrated up to the maximum load used in these tests; the maximum error in this range was 10 lb. in 4000 lb., or 0.25%. The residual-energy dynamometer had been calibrated by an absolute method. No appreciable rebound was observed throughout the tests. Since the single-shock energy absorption was in each case

TABLE XII.—Average Single-Shock and Corresponding Static Test Results.

Reference Letter :	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.
Carbon content. % :	0.12.	0.18.	0.28.	0.29.	0.33.	0.37.	0.47.	0.52.	0.58.	0.63.
Average single-shock energy. In.lb.	538	529	598	546	574	557	568	561	522	517
Static energy. In.lb.	550	616	708	674	663	723	672	688	571	550
Ratio of single-shock energy to static energy	0.97	0.865	0.854	0.808	0.862	0.77	0.845	0.84	0.91	0.94
Average single-shock extension. In.	0.243	0.235	0.182	0.197	0.203	0.176	0.167	0.155	0.121	0.113
Static extension. In.	0.26	0.249	0.197	0.205	0.21	0.19	0.164	0.159	0.115	0.115
Average single-shock reduction of area. %.	67.7	67.1	53.2	52.5	56.6	51.2	49.0	45.1	36.3	33.7
Static reduction of area. %.	68.2	67.8	54.2	55.6	54.7	51.1	47.1	44.0	32.6	34.0

less than the corresponding static energy, the difference could not be due to loss of energy at the striking surfaces. It is within the bounds of possibility that the differences in the values of the single-shock and static energies for the 0.12% and the 0.63% carbon steels were due to errors inherent in the testing technique. There is no variable, however, that would permit the few percents difference in value for the 0.12% and 0.63% carbon steels and at the same time allow for the energy difference for, say, the 0.37% carbon steel, a difference of approximately 23% between the static and single-shock values.

Referring again to Table XII., the average extensions obtained in the single-shock tests are, with the exception of those for the 0.47% and the 0.58% carbon steels, slightly less than the corresponding static values. It has been pointed out by Brown and Vincent⁽⁶⁾ that variations in elongation are more important in determining the energy absorption than variations in tensile strength. The variation between the values of reduction of area obtained by both methods of testing (Table XII.) is small and in agreement with the now generally accepted fact that there is no difference in the percentage reduction of area in the static and single-shock or impact tests.

There was no appreciable difference in the nature or appearance of the fractures of the corresponding specimens ruptured by single-shock and by static means when examined by the naked eye, except in the case of the 0.63% carbon steel; with this steel the shock fractures were dull in appearance and the static fractures had a bright crystalline appearance with a dull patch at the centre of fracture. All the specimens were cut from the same bar.

Repeated-Shock Tests.

Fig. 7 shows the nature of the curves obtained by plotting the value of the energy absorbed per shock against the number of shocks

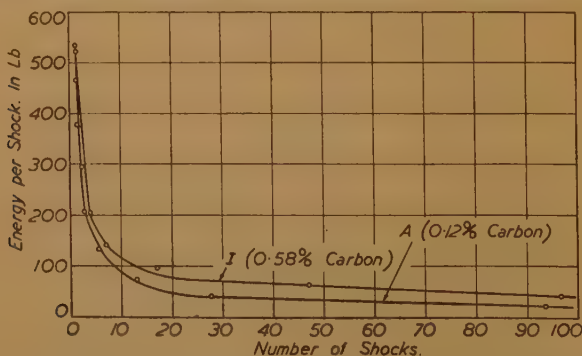


FIG. 7.—Repeated-Shock Tests. Relation of energy absorbed per shock to number of shocks for rupture.

for rupture. The two curves drawn are for the 0.12% and the 0.58% carbon steels. These curves possess the characteristics of stress endurance curves and are similar to that previously obtained for Lowmoor iron⁽¹⁾ and to those published by Stanton and Bairstow.⁽³⁾

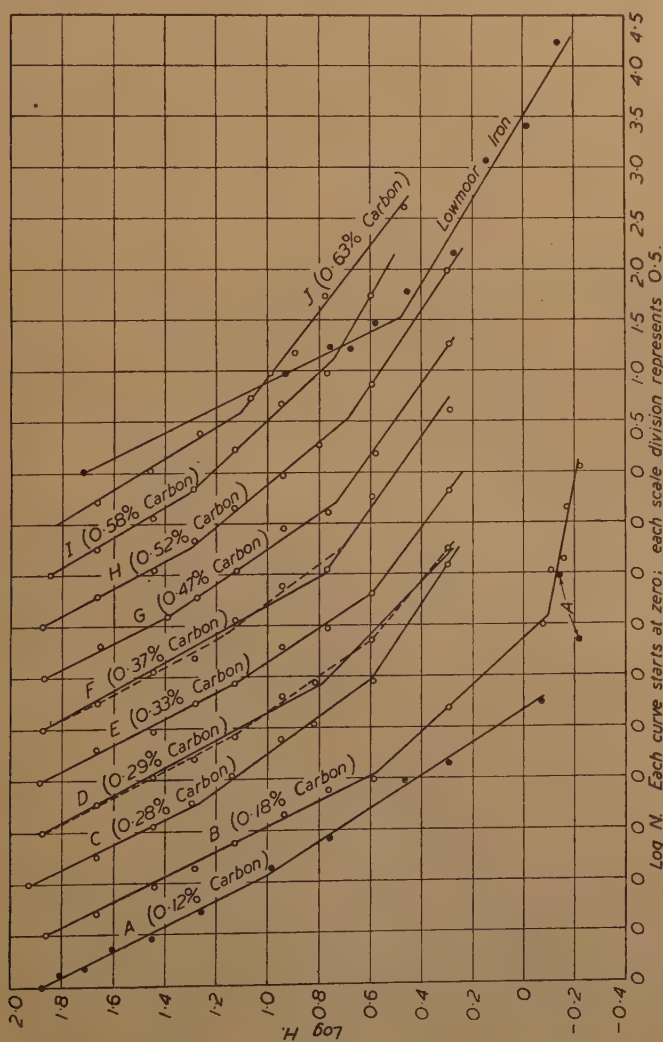


Fig. 8.—Repeated Shock Tests. Relation of height of fall of tup to number of blows to fracture.

To elucidate the properties of the steels under repeated-shock loads, curves were plotted connecting $\log H$ and $\log N$, where H

is the height of fall of the tup and N the number of blows necessary for rupture. The logarithmic curves are shown in Fig. 8, (A) to (J) ; a reproduction of the corresponding curve for Lowmoor iron ⁽¹⁾ is included. It would be possible in a few cases to draw a continuous curve which would lie evenly between the points obtained from the tests. Consideration of the relative positions of the points of stress endurance curves plotted on logarithmic paper and of the curves obtained for Lowmoor iron ⁽¹⁾ convinced the authors that straight lines through the points gave a more satisfactory curve in each case. From the individual logarithmic curves for the 0.29% and the 0.37% carbon steels it is impossible to determine, unless by additional tests, whether the true curves are represented by the dotted lines or the full lines. Examination of the other curves suggests, however, that the dotted lines represent the true curves for these two steels.

To facilitate comparison of the relative energies of the shocks required to fracture specimens of the steels after a given number of blows Fig. 9 was prepared. In the single-shock tests the energy

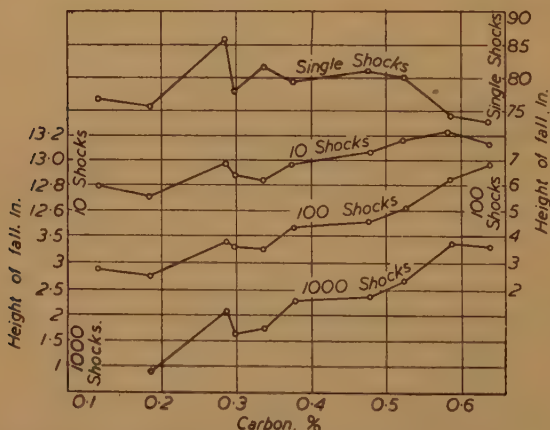


Fig. 9.—Comparison of Relative Energies of Shocks required for Fracture after a given number of blows.

required to fracture the hardest steel was slightly less than that required to fracture the softest steel. Fig. 9 reveals, however, that in tests consisting of as few as ten shocks for rupture the energy absorbed per shock is greater for the 0.63% than for the 0.12% carbon steel. In general, as the number of shocks for rupture increases, the characteristics of the single-shock curve are replaced by characteristics more akin to the values of the proof resiliences of the materials. This is in agreement with the results of Stanton and Bairstow ⁽³⁾ for bending impact tests on notched

specimens, though the method of testing here adopted appears to lay more emphasis on this reversal of characteristics and to bring it about in a smaller number of shocks.

Observation of the changes in slope of each curve, especially in the case of the 0.18% carbon steel (Fig. 8 (B)), gives rise to speculation as to whether each curve will eventually become parallel to the N axis and thus give an endurance limit for each material under these conditions. It was assumed by Stanton and Bairstow, probably from the asymptotic nature of the curves and the similarity which exists between curves derived from repeated-impact and stress endurance tests, that a limiting resistance to impact did exist. This assumption was substantiated by some repeated-impact tests carried out by them in conjunction with microscopic examination. It seems, however, that conclusive evidence of the same nature as that in existence for gradually applied stress fatigue limits is still lacking. Further, if such limits do exist, it has yet to be determined whether values obtained by using plain specimens would arrange materials in the same order as values found when using notched specimens.

Referring to the "total energy for rupture" columns in Tables II. to XI., there is a drop in value of the total energy between two consistent adjacent values in several cases. The amount of eccentricity was small in each case, a matter of a few percents. To determine whether this was due to lack of homogeneity in the materials or whether there are critical values in the total-energy range, values covering the range tested were taken from the $\log H / \log N$ curves of the materials in question and a series of total energies for rupture was estimated from those values.

The values of total energy so obtained were consistent, and when plotted against the energy per shock gave smooth curves, as indicated by the curves for the 0.12% and the 0.28% carbon steels shown in Fig. 10. The reasonable conclusion is that the observed inconsistencies were due to lack of homogeneity in the materials. Incidentally, the curves in Fig. 10 are an additional indication that the logarithmic $H-N$ curves are correct as drawn. The total-energy curves are also, of course, of an asymptotic nature and emphasise the possibility of a limiting range of energy.

It is not within the scope of this paper to prove beyond doubt the existence of limiting ranges of energy for the steels tested or to determine values of these limits. The characteristics of the $H-N$ curves, however, and the consistent way in which the logarithmic $H-N$ curves tend to become parallel to the N axis point the way to an investigation of the effects of repeated shock-stress applied to a similar family of steels when the stresses involved are of the same order as the elastic limits of the materials as found by static means.

The authors are at present engaged on the design of a high-speed machine suitable for such an investigation.

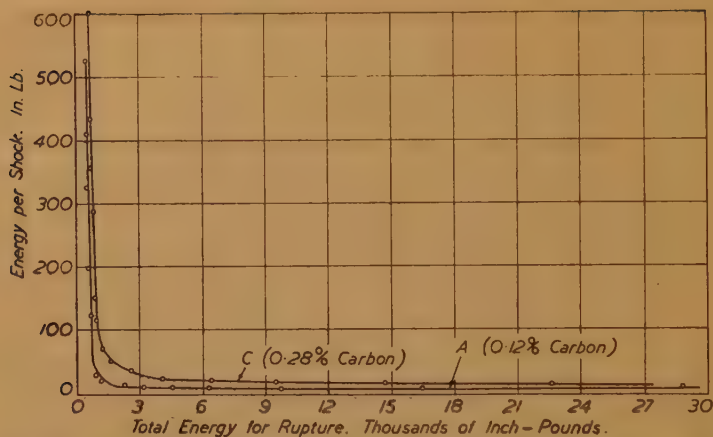


FIG. 10.—Relation of Energy Absorbed per Shock to Total Energy for Rupture.

Ductility of the Steels under Repeated Shock.

Fig. 11 was prepared to illustrate the relative ductilities of the steels tested. It is of interest to note how in each case the total extension increases slowly with a decrease in height of fall of the

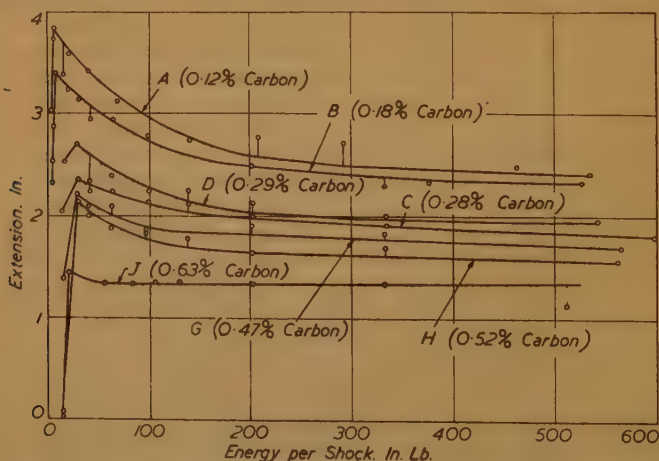


FIG. 11.—Relation of Extension to Energy Absorbed per Shock.

tup or energy per shock until a maximum is reached. From the points of maximum total extension the curves fall away rapidly as the height of fall is further decreased. Unfortunately, sufficient data are not available at present to determine whether the energy

represented by the value of H at which maximum total extension takes place has any direct connection with either the proof resilience or the work done in straining the specimen up to the yield stress. It is sufficient to state at this stage in the work that as the energy per shock approaches the proof resilience of the gauge-length of the specimen the total extension decreases rapidly in value. This value of maximum extension suggests a starting point for tests in connection with the determination of the limiting ranges of energy.

It will be seen from Tables II. to XI. that the maximum extension and a corresponding maximum reduction in area take place at approximately the same value of energy per shock. The difference between the static extension and the maximum total or resultant extension under repeated shock decreases with the carbon content of the steel, and varies between approximately 20% and 50% for the specimens tested. The difference between the static reduction of area and the maximum resultant reduction of area under repeated shock varies in a similar way between limits of approximately 3% and 15%. The appearance of the fractures of the 0.12% carbon steel was similar throughout the tests on this steel. For the range of steels from 0.18% to 0.52% of carbon the fractures were more ragged and the cone and cup less defined as the height of fall decreased. For the 0.58% and the 0.63% carbon steels an area, bright crystalline in appearance, increased with decrease in height of fall until the plane of fracture was completely crystalline in appearance. When the height of fall represented an amount of energy approaching the proof resilience, cleavage planes, at right angles to the centre-line of the specimen, were clearly visible in several cases. It is worthy of note that the great majority of the specimens fractured at the centre of the gauge-length, even when cleavage was apparent at other planes.

Conclusions.

From a survey of the work described the following points appear to be of primary importance :

(1) The ratio of the single-shock energy to the static energy varies with the carbon content of the steel.

(2) The elongation of a specimen of carbon steel when ruptured by a tensile shock may be less than the static elongation, while the reduction of area does not vary with the method of testing.

(3) From the nature of the tensile shock endurance curves there appears to be a limiting range of energy which may be applied an unlimited number of times without causing rupture.

(4) In a multi-shock test, as the number of shocks to cause rupture increases, the resultant extension and reduction of area increase to a maximum at the same value of energy absorption per shock. Further increase in the number of shocks to cause rupture is accompanied by a rapid decrease in both values of ductility.

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TESSELLATED STRESSES.—PART II.¹

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SUMMARY.

Results of recent investigations of structural tessellated stresses in materials consisting of components with different elastic constants are discussed, with special reference to cast and malleable iron.

The question of strain energy due to tessellated stresses is studied, with particular regard to phase transformation.

Tessellated stresses in the free surface are carefully analysed, and their possible rôle in connection with damping and surface deficiency in fatigue is pointed out.

INTRODUCTION.

As frequent references will be made in this paper to the previous publication, "Tessellated Stresses—Part I.,"² the numberings of equations, Tables and diagrams given in this paper are continued from those in Part I., so that all references to equations (1) to (7), Tables I. to III. and Figs. 1 to 7 are to those in Part I.

Amongst other things, more exact solutions have been found to the problems of tessellated stresses in aggregates of laminated structures and aggregates of compound spherical or compound cylindrical units, the components of which have different elastic constants. Equations (1) and (3) and Table I. are therefore of restricted application and are to be replaced by equations (8) and (9) and Tables IV. and V. of the present paper, as will be explained later.

LIST OF ADDITIONAL SYMBOLS.

The notation of the present paper is mostly in accordance with that used in Part I., but one modification has been made, and the additional symbols given in the following list are used :

List of Symbols in addition to those used in Part I.

p_j = radial stress at the junction r_j in compound cylinders—see Fig. 9 (replaces p of Part I.).

p_s = radial stress on the outer surface of a compound cylinder—see Fig. 9.

p = the external radial stress, which is also the tangential stress, on the two caps of capped cylinders—see Fig. 11.

q = stress in the axial direction of a capped cylinder—see Fig. 11; also used for the stress at right angles to lamellæ in laminated structures—see Fig. 8.

ϵ = strain.

m = the reciprocal of Poisson's ratio for an aggregate.

U = strain energy per unit volume.

¹ Received January 1, 1943.

² *Journal of The Iron and Steel Institute*, 1943, No. I., pp. 173 P–199 P.

α = linear coefficient of thermal expansion of an aggregate.

ϕ = angle between the direction of applied force and the normal to the plane of lamination.

ψ = angle between the direction of maximum strain, ϵ_{\max} , and a normal to the plane of lamination.

$[]_{+1}$ denotes a tessellated stress set up by a unit of applied stress.

I, II, III = system of rectangular co-ordinates.

x, y, z = system of rectangular co-ordinates.

Suffixes to Physical Constants.

α = a direction perpendicular to the lamellæ.

β = a direction parallel to the lamellæ.

Suffixes to Stresses.

I = stress develops in direction I only.

$(II-III)$ = stress is the same in all directions in the II, III plane.

$II(III)$ = stress develops in either direction II or direction III .

Suffixes indicating the Type of Intersecting Face.

α = perpendicular to the lamellæ.

β = parallel to the lamellæ.

TESSELLATED STRESSES IN AGGREGATES THE COMPONENTS OF WHICH HAVE DIFFERENT ELASTIC CONSTANTS.

If structural tessellated stresses develop in accordance with equation (1) in a single laminated slab the components of which have different elastic constants, the coefficient of linear expansion in

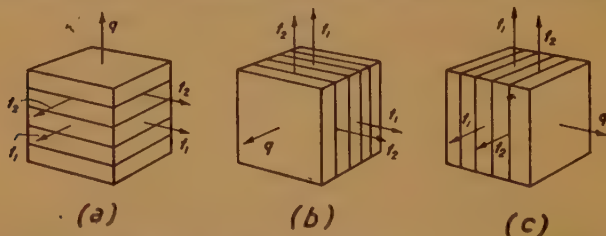


FIG. 8.—Tessellated Stresses in Laminated Cubes at Random.

directions parallel to the planes of the lamellæ will not be the same as in a direction perpendicular to them. In a compound cylindrical unit too, considered in equation (3), the coefficient of expansion of the unit in the axial direction will differ from that in directions at right angles to the axis. Statistical considerations, however, require that in random aggregates the apparent outer "strain" of a unit of tessellation should be the same in every direction. This implies the existence of a lateral stress q on the laminated slabs, see Fig. 8, and of a radial hydrostatic stress p_s on the outer diameter of compound cylinders, see Fig. 9. The analysis of tessellated stress in aggregates will now be made for strain potentials due to thermal expansion, but equation (6) should also be remembered in connection with problems of selective volume change at constant temperature.

(1) *Lamellar Structure*.—Let the random aggregate be represented by a group of three laminated cubes with lamellæ parallel to a face and with edges of unit length, in the three principal positions as shown in Fig. 8. If the linear coefficient of expansion of the aggregate be the same in all directions and denoted by α , the values of the four unknowns α , f_1 , f_2 , and q due to a change of temperature by t° C. are obtained from the equations :

$$\left. \begin{aligned} \alpha t &= \alpha_1 t + \frac{m_1 - 1}{m_1 E_1} f_1 - \frac{q}{m_1 E_1} \\ \alpha t &= \alpha_2 t + \frac{m_2 - 1}{m_2 E_2} f_2 - \frac{q}{m_2 E_2} \\ \alpha t &= u_1 \alpha_1 t + u_2 \alpha_2 t + \left(\frac{u_1}{E_1} + \frac{u_2}{E_2} \right) q - \frac{2u_1 f_1}{m_1 E_1} - \frac{2u_2 f_2}{m_2 E_2} \\ 2(u_1 f_1 + u_2 f_2) + q &= 0 \end{aligned} \right\} \quad (8)$$

The last equation of this set expresses the condition of equilibrium against translation of the representative group of three cubes. Equations (8) replace equations (1). If $m_1 = m_2 = m$ and $E_1 = E_2 = E$, q becomes zero, and equations (1a) ensue from equations (8).

(2) *Compound Cylinders*.—The random aggregate is represented by three compound cylinders of unit axial length and unit external cross-sectional area, i.e., $\pi r_s^2 = 1$ and $\pi r_j^2 = w_i$, in the three principal positions, see Fig. 9. The stresses and the coefficient α of linear

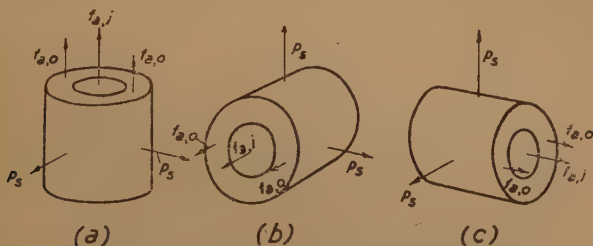


FIG. 9.—Tessellated Stresses in Compound Cylinders at Random.

thermal expansion of the aggregate due to a change of temperature by t are found from the equations :

$$\left. \begin{aligned} \alpha t &= \alpha_i t + \frac{f_{a,i}}{E_i} - \frac{2p_j}{m_i E_i} \\ \alpha t &= \alpha_o t + \frac{f_{a,o}}{E_o} - \frac{f_{t,o} + p_j}{m_o E_o} \\ \alpha t &= \alpha_o t + \frac{f_{t,o}}{E_o} - \frac{f_{a,o} + p_j}{m_o E_o} \\ (\alpha_{j,t}) \alpha_i t &+ \frac{m_i - 1}{m_i E_i} p_j - \frac{f_{a,i}}{m_i E_i} = \alpha_o t + \frac{f_{t,o}}{E_o} - \frac{f_{a,o} + p_j}{m_o E_o} \\ f_{t,o} &= \frac{2}{1 - w_i} p_s - \frac{1 + w_i}{1 - w_i} p_j; \quad f_{t,o} = \frac{1 + w_i}{1 - w_i} p_s - \frac{2w_i}{1 - w_i} p_j \\ w_i f_{a,i} + (1 - w_i) f_{a,o} + \frac{4}{\sqrt{\pi}} p_s &= 0, \end{aligned} \right\} \quad (9)$$

The last equation of this set expresses the condition for equilibrium of the representative group of units of Fig. 9 in the direction of the axis of any one of the cylinders. For $w_i = 0$, p_s becomes zero and equations (9) reduce to equations (3). If the two components of the compound cylinder have the same elastic constants equations (9) become equations (3a).

(3) *Compound Spheres and Capped Cylinders.*—Compound spheres will be treated alternately as pseudo-spherical units, viz., capped cylinders, as shown in detail in Figs. 10 and 11. The fractional volumes of the inner and outer components are the same as those of the compound sphere under consideration. As

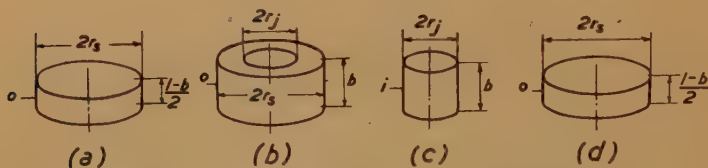


FIG. 10.—Components of Capped Cylinders.

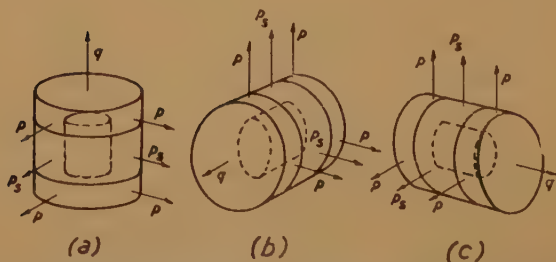


FIG. 11.—Tessellated Stresses in Capped Cylinders at Random.

$v_i + v_o = 1$, the capped cylinder has unit overall length and unit cross-sectional area, or $\pi r_s^2 = 1$; the inner cylinder has volume v_i , its length $b = v_i^{1/3}$ and its cross-sectional area $\pi r_j^2 = v_i^{2/3} = b^2$. The compound cylindrical central portion is subjected to the stresses p_j , p_s , $f_{a,i}$ and $f_{a,o}$, while the two circular caps are subjected to the external radial stress p and the uniform axial stress q (p is, at any point of the caps, both the radial and tangential stress). The random aggregate of capped cylinders of unit overall length is represented by the group of three shown in Fig. 11. It is then found that the following relations hold :

$$\left. \begin{aligned}
 at &= a_o t + \frac{f_{i,os}}{E_o} - \frac{f_{a,o} + p_s}{m_o E_o} = \frac{m_o - 1}{m_o E_o} p - \frac{q}{m_o E_o} + a_o t \\
 at &= a_o t + (1 - b) \left(\frac{q}{E_o} - \frac{2p}{m_o E_o} \right) + b \left(\frac{f_{a,o}}{E_o} - \frac{f_{i,os} + p_s}{m_o E_o} \right) \\
 (a_{j,s} t) a_i t &+ \frac{f_{a,i}}{E_i} - \frac{2p_j}{m_i E_i} = a_o t + \frac{f_{a,o}}{E_o} - \frac{f_{i,os} + p_j}{m_o E_o} \\
 (a_{j,i} t) a_i t &+ \frac{m_i - 1}{m_i E_i} p_j - \frac{f_{a,i}}{m_i E_i} = a_o t + \frac{f_{i,os}}{E_o} - \frac{f_{a,o} + p_j}{m_o E_o} \\
 f_{i,os} &= \frac{2}{1 - b^2} p_s - \frac{1 + b^2}{1 - b^2} p_j; \quad f_{i,os} = \frac{1 + b^2}{1 - b^2} p_s - \frac{2b^2}{1 - b^2} p_j \\
 q &= b^2 f_{a,i} + (1 - b^2) f_{a,o} \\
 \frac{4b}{\sqrt{\pi}} p_s &+ \frac{4}{\sqrt{\pi}} (1 - b) p + q = 0.
 \end{aligned} \right\} \quad (10)$$

The last equations were derived in the same way as the last one in set (9). If the aggregate is made up of components with the same elastic constants, *e.g.*, as in a spheroidised steel, q becomes zero, *i.e.*, the stress system of each unit of tessellation is self-compensated just as with laminated slabs and compound cylinders. It is also seen that :

$$\alpha = b^3 a_i + (1 - b^3) a_o, \text{ and } f_{red,os} = |f_{i,os} - p_j| = \frac{mE}{m - 1} (a_o - a_i) t,$$

which seems to confirm the correctness of treating a compound sphere as a "capped cylinder."

SURFACE INTERSECTIONS.

Since stresses cannot develop at right angles to a free surface, surface intersections are subjected to two-dimensional stress conditions in the plane of the surface layer. The following approximate method of analysis suggests itself : Determine the size and shape of the outer contour of a certain section through the unit that would actually develop in a unit inside the body owing to the strain potential. Cut a slice of elementary thickness out of the unit at that section, subject it to the actual strain potential, in addition force its outer contour into the size and shape previously found, and determine the stresses required to produce this combination of strains.

(1) *Laminated Slabs*.—Two significant cases have been investigated, one in which the free surface is at right angles (suffix α) to the laminations and the other with the free surface parallel (suffix β) to the lamellæ.

The stresses in a free surface at right angles to the lamellæ are given by the equations :

$$\left. \begin{aligned}
 at &= a_1 t + \frac{f_{1,\alpha}}{E_1} - \frac{q_\alpha}{m_1 E_1} = a_2 t + \frac{f_{2,\alpha}}{E_2} - \frac{q_\alpha}{m_2 E_2} \\
 at &= u_1 a_1 t + u_2 a_2 t + \left(\frac{u_1}{E_1} + \frac{u_2}{E_2} \right) q_\alpha - \frac{u_1 f_{1,\alpha}}{m_1 E_1} - \frac{u_2 f_{2,\alpha}}{m_2 E_2}
 \end{aligned} \right\} \quad (11)$$

where a is the coefficient of expansion of the aggregate as calculated from equations (8). If the two components have the same elastic

constants, the factor of relaxation is independent of the volume fraction of the components, being uniformly $\frac{m-1}{m}$ for $f_{1,a}$ and $f_{2,a}$, while $q = 0$ in this case, both inside and outside the body.

For intersection parallel to the lamellae, $q_\beta = 0$, and the stresses in the free surface are found from the equations :

$$\left. \begin{aligned} at &= a_1 t + \frac{m_1 - 1}{m_1 E_1} f_{1,\beta} \\ at &= a_2 t + \frac{m_2 - 1}{m_2 E_2} f_{2,\beta} \end{aligned} \right\} \dots \dots \dots (12)$$

If the components have the same elastic constants, $f_{1,\beta} = f_1$ and $f_{2,\beta} = f_2$, i.e., no relaxation occurs in such an intersecting face. The pearlite of steel is a good example of a laminated structure with components having the same elastic constants.

(2) *Spherical and Cylindrical Units*.—The significant types of intersection which have been investigated are shown in Figs. 12, (a), (b) and (c). Fig. 12(d) shows the radial surface stresses concerned. The surface stresses in an intersecting face of the type shown in Fig. 12(a) can be calculated from the equations :

$$\left. \begin{aligned} at &= a_o t + \frac{f_{i,os}}{E_o} - \frac{p_i}{m_o E_o} \\ (a_{j,t} =) a_j t + \frac{m_i - 1}{m_i E_i} p_j &= a_o t + \frac{f_{i,oj}}{E_o} - \frac{p_j}{m_o E_o} \\ f_{i,oj} &= \frac{2}{1-b^2} p_i - \frac{1+b^2}{1-b^2} p_j; f_{i,os} = \frac{1+b^2}{1-b^2} p_i - \frac{2b^2}{1-b^2} p_j \end{aligned} \right\} \dots \dots (13)$$

where a , the coefficient of expansion of the aggregate, is equal to $a_o + \frac{1}{t} \cdot \frac{m_o - 1}{m_o E_o} f_{i,os}$ from equations (2); b^2 is the area of the inner component expressed as a fraction of the total area of the intersecting face, and is equal to $v_i^{\frac{2}{3}}$, where v_i is the fractional volume of the inner component of a compound sphere.

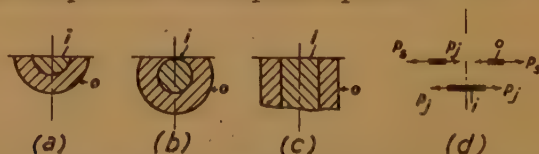


FIG. 12.—Modes of Significant Intersections with Compound Spheres and Cylinders.

The set of equations (13) applies also to the type of intersection shown in Fig. 12(b), for which b^2 must be put equal to zero, and to the type shown in Fig. 12(c), for which a is found from equations (9) and b^2 is numerically equal to w_i , the volume fraction of the inner component in a compound cylinder.

It is now seen, from the second expression in equations (13), that when the two components have the same elastic constants the yield

potential, $f_{red,oj} = |f_{t,oj} - p_j|$, becomes $E(a_o - a_i)t$ in both types of intersection of compound spheres, i.e., the factor of stress relaxation is again $\frac{m-1}{m}$ as with laminated slabs or compound cylinders, Fig. 12(c). It may be accepted, therefore, that equations (13) give at least for $f_{red,oj}$ a fairly correct value in cases of surface intersection of compound spheres in general.

The representation of the intersection of a compound sphere by a "compound cylindrical film" involves the substitution of inversely quadratic expressions for inversely cubic ones as regards the tangential and radial stresses.

(3) *Strains in Surface Intersections.*—It is found that the components of the "surface film" cut out of a unit occupy different proportions of its total area when subjected to the above-mentioned combination of strains from what they would in a unit inside the body which is subjected only to the strain potential of tessellation. That means that the components of intersected units are subjected to special distortion near the free surface, as is indicated to a greatly



FIG. 13.—Particular Strains near Surface Intersections.

exaggerated extent in Figs. 13, (a) to (c), for laminated, spherical and cylindrical tessellation, respectively. Whether a lamella is increased or reduced in width or the core component of a compound sphere or cylinder spreads or contracts at the free surface depends on the actual physical constants of the components and the type of tessellation. This phenomenon develops even when the components have the same elastic constants, in general, and is one of the reasons why it is suggested that equations (11) to (13) are approximate only. Exact mathematical analysis should disclose whether or not the distortion indicated by Fig. 13 has any repercussion on the degree of relaxation found by equations (11) to (13).

STRUCTURAL TESSELLATED STRESSES DUE TO EXTERNAL FORCES.

It is to be emphasised that tessellated stresses due to external forces only would not develop if the structural components had the same elastic constants; they would, however, develop in porous bodies. For simplicity's sake, not the tessellated stresses themselves but the system combined with the "external" one will be analysed.

(1) *Laminated Slabs.*—Let the random aggregate be represented by cubes, laminated parallel to a face, with edges of unit length, in the three principal positions, so that one axis of symmetry of the cubes is parallel to the direction I of the simple average stress f due to the

external force applied, as shown in Fig. 14. For convenience of notation a system of co-ordinates *I, II, III* is chosen. The analysis is

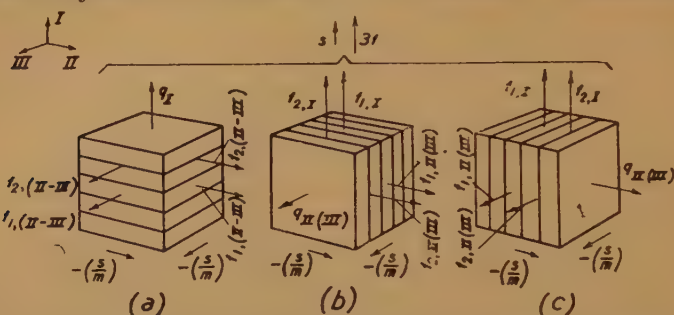


FIG. 14.—Laminated Cubes at Random subjected to External Stress f .

based on the consideration that all cubes of the "random" system, Fig. 14, must undergo the same longitudinal strain, $s = \frac{f}{E}$, in the

direction *I*, and also the same lateral strain, $-\left(\frac{s}{m}\right)$, in both lateral directions, viz., *II* and *III*, where E and m denote the elastic constants of the laminated body as a whole. While the suffixes 1 and 2 refer to the component materials, suffix *I* in addition indicates that a certain stress develops only in the direction *I*, suffix (*II-III*) means that the stress is the same in all directions in the (*II-III*) plane, and suffix *II(III)* denotes that the stress develops in either the direction *II* or the direction *III*. The stress system is fully determined by the following equations :

$$\left. \begin{aligned} s &= \left(\frac{u_1}{E_1} + \frac{u_2}{E_2} \right) q_I - 2u_1 \frac{f_{1,II-III}}{m_1 E_1} - 2u_2 \frac{f_{2,II-III}}{m_2 E_2} \\ s &= \frac{f_{1,I}}{E_1} - \frac{f_{1,II(III)} + q_{II(III)}}{m_1 E_1} = \frac{f_{2,I}}{E_2} - \frac{f_{2,II(III)} + q_{II(III)}}{m_2 E_2} \\ -\left(\frac{s}{m} \right) &= \frac{m_1 - 1}{m_1 E_1} f_{1,II-III} - \frac{q_I}{m_1 E_1} = \frac{m_2 - 1}{m_2 E_2} f_{2,II-III} - \frac{q_I}{m_2 E_2} \\ -\left(\frac{s}{m} \right) &= \frac{f_{1,II(III)}}{E_1} - \frac{f_{1,I} + q_{II(III)}}{m_1 E_1} = \frac{f_{2,II(III)}}{E_2} - \frac{f_{2,I} + q_{II(III)}}{m_2 E_2} \\ -\left(\frac{s}{m} \right) &= \left(\frac{u_1}{E_1} + \frac{u_2}{E_2} \right) q_{II(III)} - u_1 \frac{f_{1,I} + f_{1,II(III)}}{m_1 E_1} - u_2 \frac{f_{2,I} + f_{2,II(III)}}{m_2 E_2} \\ u_1(f_{1,II-III} + f_{1,II(III)}) + u_2(f_{2,II-III} + f_{2,II(III)}) + q_{II(III)} &= 0 \\ 2u_1 f_{1,I} + 2u_2 f_{2,I} + q_I &= 3f \end{aligned} \right\} \quad (14)$$

The elastic constants of the aggregate are, of course, $E = \frac{f}{s}$ and

$$\frac{1}{m} = \frac{\left(\frac{s}{m} \right)}{s}.$$

If lamellæ the normal *Z* to which makes the angle ϕ with the

direction I of the "external stress" f are concerned, it is convenient to investigate a laminated cube with edges of unit length and orientated parallel to the system I - III , with one dimension obliquely laminated at an angle ϕ , as shown in Fig. 15. It is required that this

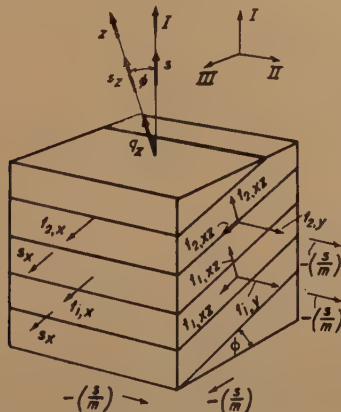


FIG. 15.—Obliquely Laminated Cube subjected to External Stress f .

cube should have the bulk strain s in direction I , and $-\left(\frac{s}{m}\right)$ in the plane (II - III), the values of which are to be determined by solving equations (14). Introducing the system of co-ordinates x, y, z for the strains and stresses in the oblique lamellæ, as shown in Fig. 14, it is apparent that shear strain and stress develop only in the xz plane. The direct strains s_x and s_y and the shear strain s_{xz} are each the same in both components of the lamellæ; furthermore, $s_y = -\left(\frac{s}{m}\right)$; s_z , however, is a bulk value over the cube as a whole. The shear stresses in the lamellæ 1 and 2 are denoted by $f_{1,xz}$ and $f_{2,xz}$, respectively. The values may be found from the equations :

$$\left. \begin{aligned} s &= s_x \sin^2 \phi + s_z \cos^2 \phi + \frac{s_{xz}}{2} \sin 2\phi \\ -\left(\frac{s}{m}\right) &= s_x \cos^2 \phi + s_z \sin^2 \phi - \frac{s_{xz}}{2} \sin 2\phi \\ -\left(\frac{s}{m}\right) &= \left(\cos^2 \phi + \frac{\sin 2\phi}{2}\right) s_x + \left(\sin^2 \phi - \frac{\sin 2\phi}{2}\right) s_z + (\cos 2\phi - \sin 2\phi) \frac{s_{xz}}{2} \\ s_x &= \frac{f_{1,x}}{E_1} - \frac{q_z + f_{1,y}}{m_1 E_1} = \frac{f_{2,x}}{E_2} - \frac{q_z + f_{2,y}}{m_2 E_2} \\ -\left(\frac{s}{m}\right) = s_y &= \frac{f_{1,y}}{E_1} - \frac{q_z + f_{1,x}}{m_1 E_1} = \frac{f_{2,y}}{E_2} - \frac{q_z + f_{2,x}}{m_2 E_2} \\ s_z &= \left(\frac{u_1}{E_1} + \frac{u_2}{E_2}\right) q_z - u_1 \left(\frac{f_{1,x} + f_{1,y}}{m_1 E_1}\right) - u_2 \left(\frac{f_{2,x} + f_{2,y}}{m_2 E_2}\right) \end{aligned} \right\} \quad (15)$$

These read in terms of the representative figures of equations (14):

$$\left. \begin{aligned}
 s_x &= \frac{m-1}{2m} s - \frac{m+1}{2m} s \cos 2\phi; \quad s_y = -\left(\frac{s}{m}\right); \quad s_z = \frac{m-1}{2m} s + \frac{m+1}{2m} s \cos 2\phi \\
 s_{xx} &= \frac{m+1}{m} s \sin 2\phi; \quad q_x = \frac{q_{II(II)} + q_I}{2} - \frac{q_{II(II)} - q_I}{2} \cos 2\phi \\
 f_{1,x} &= \frac{f_{1,I} + f_{1,II(II)}}{2} - \frac{f_{1,I} - f_{1,II(II)}}{2} \cos 2\phi \\
 f_{2,x} &= \frac{f_{2,I} + f_{2,II(II)}}{2} - \frac{f_{2,I} - f_{2,II(II)}}{2} \cos 2\phi \\
 f_{1,y} &= \frac{f_{1,II(II)} + f_{1,II(II)}}{2} - \frac{f_{1,II(II)} - f_{1,II(II)}}{2} \cos 2\phi \\
 f_{2,y} &= \frac{f_{2,II(II)} + f_{2,II(II)}}{2} - \frac{f_{2,II(II)} - f_{2,II(II)}}{2} \cos 2\phi \\
 f_{1,z} &= \frac{m+1}{m} s G_1 \sin 2\phi; \quad f_{2,z} = \frac{m+1}{m} s G_2 \sin 2\phi
 \end{aligned} \right\} (16)$$

where $G_1 = \frac{m_1}{2(m_1+1)} E_1$ and $G_2 = \frac{m_2}{2(m_2+1)} E_2$ are the moduli of rigidity of the two components.

Stresses in surface intersections depend on the strains in the surface at the point under consideration. In lamellæ parallel to the surface no shear stress develops and a solution can be found on the lines of equations (12). If free surfaces perpendicular to the lamellæ are under consideration a possible method of determining the stresses set up in them by an applied force is as follows: The maximum values of the surface strains s_{\max} and s_{\min} caused by the applied force are determined by applying the theory of elasticity. Let ψ be the angle between the normal to the lamellæ and the direction of s_{\max} ; then a set of equations of the type of equations (15) can be obtained, where, among other modifications, ψ is to be substituted for ϕ and s_{\max} and s_{\min} for s and $-\left(\frac{s}{m}\right)$, respectively.

(2) *Spherical Tessellation*.—An approximate analysis may be obtained from a consideration of the stresses developed in a capped cylinder subjected to an external force. The units, Fig. 11, are all considered to have their cylinder axes parallel to the simple "external stress" f , which is here the axial stress applied to the covers instead of q in equations (10). With the notation $b^3 = v_i$ for the volume fraction of the core component, the solution is calculated from the equations:

$$\left. \begin{aligned}
 \frac{f_{a,i}}{E_i} - \frac{2p_j}{m_i E_i} &= \frac{f_{a,o}}{E_o} - \frac{f_{i,o} + p_j}{m_o E_o}; \quad \frac{m_i - 1}{m_i E_i} p_j - \frac{f_{a,i}}{m_i E_i} = \frac{f_{i,o}}{E_o} - \frac{f_{a,o} + p_j}{m_o E_o} \\
 -\left(\frac{s}{m}\right) &= \frac{f_{i,o}}{E_o} - \frac{f_{a,o} + p_s}{m_o E_o} = \frac{m_o - 1}{m_o E_o} p - \frac{f}{m_o E_o} \\
 b^2 f_{a,i} + (1 - b^2) f_{a,o} &= f; \quad b p_s + (1 - b) p = 0 \\
 s &= b \left(\frac{f_{a,o}}{E_o} - \frac{f_{i,o} + p_s}{m_o E_o} \right) + (1 - b) \left(\frac{f}{E_o} - \frac{2p}{m_o E_o} \right) \\
 f_{i,o} &= \frac{2}{1 - b^2} p_s - \frac{1 + b^2}{1 - b^2} p_j; \quad f_{i,o} = \frac{1 + b^2}{1 - b^2} p_s - \frac{2b^2}{1 - b^2} p_j
 \end{aligned} \right\} \quad (17)$$

and the elastic constants of the aggregate are $E = \frac{f}{s}$ and

$$\frac{1}{m} = \frac{\left(\frac{s}{m}\right)}{s}.$$

(3) *Porous Solids*.—The formulæ required are developed in the same way as those given in equations (17). The volume fraction of the voids is denoted by b^3 ; the material itself is the "outer" component and, as usual, its elastic constants and the stresses developed in it have the suffix o . Since $p_j = 0$ and $f_{a,i} = 0$, the required formulæ are:

$$\left. \begin{aligned} -\left(\frac{s}{m}\right) &= \frac{f_{i,os}}{E_o} - \frac{f_{a,o} + p_s}{m_o E_o} = \frac{m_o - 1}{m_o E_o} p - \frac{f}{m_o E_o} \\ (1 - b^2)f_{a,o} &= f; \quad b p_s + (1 - b)p = 0 \\ s &= b \left(\frac{f_{a,o}}{E_o} - \frac{f_{i,os} + p_s}{m_o E_o} \right) + (1 - b) \left(\frac{f}{E_o} - \frac{2p}{m_o E_o} \right) \\ f_{i,oj} &= \frac{2}{1 - b^2} p_s; \quad f_{i,os} = \frac{1 + b^2}{1 - b^2} p_s; \quad E = \frac{f}{s}; \quad \frac{1}{m} = \frac{\left(\frac{s}{m}\right)}{s} \end{aligned} \right\} \quad (18)$$

STRESS CONCENTRATION.

For systems of spherical tessellation, or plain or capped cylinders at random, the yield potential $f_{red,oj}$ accounts, in a statistical sense, for the stress concentration due to tessellated stresses.

For lamellar structures at random, however, the calculations are quite deficient in this respect, since they do not consider the very great stress concentration which develops around the *edges* of lamellæ embedded in the other component. A close approximation to this stress concentration—except for the case of tessellated stresses due to external forces—may be readily obtained from the calculation of the limiting value of $f_{red,oj}$ of a compound cylinder as the fractional volume w_i of the core approaches zero, the core consisting of the material of the lamellæ under consideration. The same holds for surface intersections at right angles to the lamellæ. Similarly, the stress concentration at the "hemispherical caps" of plain compound cylinders is found from $f_{red,oj}$ for a compound sphere of $v_i = 0$.

The above consideration seems to obviate the interest in the investigation of tessellated stresses in compound ellipsoids.

No solution can be offered, for the time being, for the very considerable and extraordinarily influential stress concentration which develops, owing to external forces, around the edges of lamellæ, or with spherical tessellation, or with capped cylinders, while they are carefully accounted for when porous solids are concerned. The stresses obtained from equations (14), (16), (17) and (18) should be considered as mean values over the respective component; the elastic constant s of the aggregate, however, may be fairly exact.

STRAIN ENERGY.

The formula for the strain energy, integrated over unit volume, of lamellar structures is :

$$U = u_1 \left(\frac{m_1 - 1}{m_1 E_1} f_1^2 + \frac{q^2}{2E_1} - 2 \frac{f_1 q}{m_1 E_1} \right) + u_2 \left(\frac{m_2 - 1}{m_2 E_2} f_2^2 + \frac{q^2}{2E_2} - 2 \frac{f_2 q}{m_2 E_2} \right) \quad (19)$$

and for compound spheres :

$$U = \frac{3(m_i - 2)}{2m_i E_i} v_i p_j^2 + \left(\frac{9(m_o - 1)}{4m_o E_o} \cdot \frac{v_i}{1 - v_i} + \frac{3(m_o + 1)}{4m_o E_o} \right) v_i p_j^2 \quad (20)$$

It is noteworthy that the expression for the strain energy due to tessellated stresses with components having the same elastic constants is independent of the actual shape of the components and reads, per unit volume :

$$U = \frac{mE}{m-1} X(1-X)\lambda^2 \quad (21)$$

where X denotes the volume fraction of one of the components, $(1-X)$ that of the other, and λ the value of the actual strain potential, *e.g.*, $\lambda = (a_o - a_i)t$ for a temperature change by t degrees, or :

$$\lambda = \left[\left(\frac{\text{Specific volume of new phase}}{\text{Specific volume of old phase}} \right)^t - 1 \right] \text{ for a phase change.}$$

PHYSICAL CONSTANTS.

If structural tessellated stresses due to heating or cooling are being considered, the elastic constants that have been used for the calculation are those that correspond to the end temperature, and the thermal coefficients are the average ones for the range of temperature concerned.

For the calculation of tessellated stresses, such as those due to phase change which develop at constant temperature t_1 , the elastic constants and the figures for change in volume should be those valid at t_1 . If in such cases all the physical constants refer to a temperature t_2 , different from that at which transformation occurs, the stresses calculated are a combination of those due to the phase change at t_1 and of those due to heating or cooling from t_1 to t_2 . Consequently, as stated in Part I., the stress values given in Figs. 5 to 7 are a combination of the stresses set up by the phase change and those arising from the subsequent cooling to 20° C.

IRON AND CEMENTITE.

It is found with normalised steel cooled by 680° C. that, owing to stress concentration, a yield potential of 82,180 lb. per sq. in. develops around the edges of cementite or ferrite lamellæ in hypo- or hyper-eutectoid steel, respectively, involving the probability of plastic yield around the edges of cementite lamellæ in hypo-eutectoid steel.

In the calculation for Fig. 3 pearlite was considered as the core component of the spherical tessellation with matrices of either ferrite or cementite. This is a correct assumption in general with normalised steel, and is very convenient for purposes of discussion, since the stresses in the components of the pearlite are homogeneous. Under certain conditions, pearlite plays the rôle of matrix in the spherical tessellation with ferrite or cementite. The combined stresses in the lamellæ of pearlite then vary with the radius of the spherical system as well as with the angle which is made by the lamella with the radius vector at the point under consideration. For the above-discussed conditions, *i.e.*, for cooling by 680° C., no stress will ever exceed the yield potential of 82,180 lb. per sq. in.

The strain energy due to a drop in temperature of 680° C. is $U = 157.6X(1 - X)$, where X denotes the volume fraction of cementite. Its maximum value U_{\max} is 39.4 in.lb. per cu. in. and is found in a white cast iron containing 3.29% of carbon, corresponding to $X = 0.5$, which is free from both martensite and austenite.

GRAPHITE IN FERRITE MATRIX.

Rows 1 to 7 of Table IV. show the stresses, reduced stresses, strain energy and coefficient of linear expansion of an aggregate of lamellar graphite in ferrite, due to a drop in temperature of 680° C., calculated for both limiting values of m_g for graphite, *viz.*, 2.18 and 2.0, and for weight percentages of graphite up to 4%. Rows 1 to 6 were obtained from equations (8) and row 7 from equation (19). The yield resistance of graphite is very small; it will therefore yield, involving great reduction in f_f and f_g , until $f_{red,g} = |f_g - q|$ has become less than the yield resistance of graphite. It is apparent that the more lamellar the shape and the greater the quantity of graphite in cast iron the more will the plasticity of graphite facilitate plastic relaxation during cooling and reduce the order of magnitude of the actually resulting tessellated stresses. This plastic relaxation also causes a progressive modification of the theoretical linear coefficients of thermal expansion of the aggregate given in row 6. That plastic strain has been thoroughly studied in its effect on the microstructure of graphite.¹

Row 8 was obtained on the assumption that $\bar{a} = \frac{1}{3}(a_a + 2a_\beta)$, where a_a and a_β denote the apparent coefficients of thermal expansion—calculated for the stress system given by equation (1)—in directions perpendicular and parallel to the lamellæ of a laminated slab, respectively. \bar{U} was calculated from equation (19), again using the values of f_1 and f_2 found by equation (2). A comparison of \bar{U} and U emphatically illustrates the theoretical difference between equations (1) and (8).

¹ H. Morrogh, "The Polishing of Cast Iron Micro-Specimens and the Metallography of Graphite Flakes," *Journal of The Iron and Steel Institute*, 1941, No. I., p. 195 r, Figs. 27-33.

TABLE IV.—*Tessellated Stresses with Lamellar Graphite in Ferrite Matrix due to a Temperature Drop of 680° C.*

Row.	Stresses develop- ing—	Stresses, lb. per sq. in. Strain Energy, in. lb. per cu. in.	m_g	Graphite. Weight-%.									
				0.	0.01.	0.05.	0.1.	0.5.	1.	2.	3.	4.	
1	f_g f_f q $f_{red,g}$ $f_{red,f}$ $10^6 a$ U In interior of body.		2	-18,850	-18,968	-19,432	-20,008	-24,485	-29,755	-39,300	-47,620	-54,820	
2			2.18	-17,415	-17,503	-17,852	-18,279	-21,489	-24,995	-30,695	-36,065	-38,480	
3			2	0	+	341	683	3,466	7,040	14,470	22,175	30,070	
4			2.18	0	+	305	609	2,983	5,825	11,180	16,205	20,980	
5			2	0	123	613	1,222	2,443	4,885	9,769	14,653	19,537	
6			2.18	0	110	547	1,086	2,162	4,324	8,648	12,972	17,296	
7			2	18,850	18,845	18,819	18,786	18,518	18,185	17,825	16,885	16,365	
8	$10^6 \bar{a}$ \bar{U} In interior, (1), equation—		2	14,98	14,576	14,191	13,822	13,473	
9			2.18	14,98	14,616	14,270	13,940	13,634	
			2.18	0	6.05	9.87	14.4	18.8	
10	$f_{red,g} = f_{f,g}$ $f_{red,f} = f_{f,f} - q_g$ q_g In surface intersections— At right angles to lamellae.		2	-9,425	-9,429	-9,448	-9,467	-9,510	-9,567	-9,637	-9,721	-9,827	
11			2.18	-9,425	-9,437	-9,468	-9,501	-9,559	-9,631	-9,710	-9,804	-9,915	
12			2.18	0	+	475	946	1,891	3,782	7,564	11,346	15,128	
13			2	0	+	460	915	1,830	3,660	7,320	10,980	14,640	
14	$f_{f,g} = f_{red,g}$ $f_{f,f} = f_{red,f}$ Parallel to lamellae.		2.18	0	12	77	147	294	588	882	1,176	1,470	
15			2.18	0	29	121	229	458	916	1,374	2,061	2,748	
16			2	-18,850	-18,845	-18,819	-18,786	-18,518	-18,185	-17,825	-16,885	-16,365	
17			2.18	-17,415	-17,409	-17,387	-17,359	-17,149	-16,904	-16,469	-16,076	-15,726	
18			2	0	+	602	1,203	2,406	4,812	9,220	13,635	18,050	
19			2.18	0	103	538	1,079	2,158	4,316	8,360	12,404	16,448	

Certain stresses in surface intersections at right angles to and parallel to the lamellæ are given in rows 10 to 14; they were calculated by equations (11) and (12), using the value of a given in row 6. The stresses develop from the superposition of two stress systems: First, the internal stresses f_f , f_g and q modified by a relaxation factor which is the same for the three stresses but varies according to the type of intersection, and, second, a tension which is the same in all directions in the surface film. These and other details of the surface relaxation may be easily studied from Table IV. The real values of the surface stresses may, of course, be seriously modified by the plastic yield of graphite. The existence of the above-mentioned surface tension may account for the remarkable observation which has been made with prismatic laboratory specimens in investigations on the growth of cast iron due to the application of pulsating heating, that the specimens tend to round themselves like those of steel subjected to repeated hardening.

Rows 1 to 9 of Table V. refer to certain cooling stresses, the strain energy and the coefficient of linear expansion of *spherical* graphite in a matrix of ferrite after cooling through a temperature range of 680° C. Rows 1 to 3 were obtained from equations (2) and the $f_{t,os}$ and p_j values were used respectively to calculate a and put in equations (20) to calculate U —row 6. The stresses in intersecting faces were calculated from equations (13), and for these intersections the Table shows, tentatively, not only the apparently reliable $f_{red,oj}$ values but also those of p_j , because they represent the yield potential that would be applied to graphite in surface intersections. In the interior the spherical graphite would not yield at all, but the yield of the metallic matrix may in fact allow a degree of relaxation which increases as m_g becomes smaller. In surface intersections, however, the graphite may yield to such an extent that p_j nearly vanishes and the relaxation is considerably enhanced.

The comparison of row 5 of Table V. with row 7 of Table IV. reveals a very great reduction in the strain energy with lamellar graphite. This may be one of the reasons why temper-carbon is never exactly spherical in malleable cast iron. Since capped cylinders are a convenient form of representation of the pseudo-spherical shape, tessellated stresses with the latter system of graphite in ferrite are shown in rows 10 to 14 of Table V. Even this fairly small deviation from the exact sphere gives a noticeable reduction in the strain energy, and causes reduced shear stresses $f_{red,g}$ to be applied to the graphite. This is further evidence for the unstable character of the spherically shaped graphite in iron.

All the above calculations refer to graphite in a matrix of ferrite. If the matrix be pearlite or cementite, which have approximately the same elastic constants as ferrite, the stresses are obtained by substituting $(a_p - a_g)$ or $(a_c - a_g)$ for $(a_f - a_g)$ in the relevant formulæ, i.e., the stresses of both Tables IV. and V. are to be reduced in the ratio 11.25 : 11.61 for a pearlite matrix or in the ratio 8.79 :

TABLE V.—*Tessellated Stresses with Spherical and Pseudo-Spherical (Capped Cylinders, Suffix cc) Graphite in Ferrite Matrix due to a Temperature Drop of 680° C.*

Row.	Stresses develop- ing—	Stresses, lb. per sq. in. Strain Energy, in. lb. per cu. in.	m_g	Graphite, Weight-%.									
				0.	0.01.	0.05.	0.1.	0.5.	1.	2.	3.	4.	
1	p_j		2	-364,370	-364,168	-363,347	-362,326	-354,323	-344,750	-326,730	-310,210	-295,020	
2	$f_{i,oj} - p_j = f_{red,oj}$		2-18	-86,928	-86,917	-86,869	-86,811	-86,344	-85,765	-84,605	-87,305	-82,315	
3			2	+546,555	+546,444	+545,974	+545,391	+540,819	+538,060	+525,980	+515,610	+506,980	
4	$f_{i,cc} = f_{red,cc}$		2-18	+130,392	+130,420	+130,532	+130,672	+131,701	+133,190	+135,960	+141,455	+141,455	
5	$10^6 \alpha$		2	0	0	0	0	0	0	0	0	0	
6	$p_j = f_{red,g}$		2-18	14.98	14.9735	14.947	14.915	14.660	14.354	13.781	13.254	12.769	
7	$f_{i,oj} - p_j = f_{red,oj}$		2	14.98	14.9784	14.972	14.964	14.902	14.824	14.669	14.516	14.363	
8	$p_j = f_{red,g}$		2-18	0	0.36	1.79	3.59	17.9	34.6	66.7	96.4	124	
9	$f_{i,oj} - p_j = f_{red,oj}$		2	-17,085	-17,081	-17,016	-16,922	-16,128	-15,240	-13,680	-12,380	-11,280	
10	$p_{j,cc}$		2-18	-15,895	-15,909	-15,921	-15,925	-16,848	-15,730	-15,450	-15,170	-14,890	
11	$f_{a,i,cc} - p_{j,cc} = f_{red,g,cc}$		2	+34,169	+34,228	+34,995	+36,114	+45,530	+66,050	+74,535	+89,960	+103,065	
12	$f_{a,oj,cc} - p_{j,cc} = f_{red,oj,cc}$		2-18	+31,790	+31,618	+31,452	+31,419	+32,407	+33,920	+37,550	+41,190	+44,745	
13	$10^6 \alpha_{cc}$		2	-17,085	-17,058	-16,946	-16,804	-15,652	-14,170	-11,200	-8,180	-5,215	
14	U_{cc}		2-18	-15,895	-15,889	-15,865	-15,835	-15,590	-15,285	-14,680	-14,080	-13,480	

11.61 for a cementite matrix, and the strain energies in the ratio of the squares of these factors. Figures are also given in Tables IV. and V. for some fractions of 1% of graphite, since they may be of interest in connection with transformer sheets and the unintentional graphitisation of steel of moderate carbon percentage.

It is apparent that the existence of a lateral stress q in the laminated tessellation of graphite with a ferrous matrix does not affect in any way the metallurgical inferences which have been made previously with regard to problems connected with iron, graphite and cementite.

Concerning the application of external forces to cast iron and the tessellated stresses set up by them, equations (16) reveal that stresses in an "obliquely laminated" slab are governed exclusively by the angle of obliquity and by the tessellated stresses found in the slabs of "principal orientation" as shown in Fig. 15; the greatest stresses develop in the latter and are found by equations (14). The investigation is therefore restricted to stresses in lamellæ parallel to and at right angles to the external force. It is convenient to calculate them for unit axial tension, using the notation $\frac{f_{f,I}}{f} = [f_{f,I}]_{+1}$, and to call them "principal load factors per unit area." The "theoretical" stresses will then be given by the product of these factors and the actual average stress f , with a suitable factor to allow for stress concentration.

The results are shown in Table VI. for the limiting values of m_g , viz., 2 and 2.18. Since the elastic constants of ferrite and

TABLE VI.—*Principal Load Factors per Unit Area and Bulk Elastic Constants with Lamellar Graphite in Ferrous Matrix for Tessellated Stresses due to Application of External Force.*

Row.	Principal Load Factors and Bulk Elastic Constants.	m_g .	Lamellar Graphite. Weight-%.					
			0.	1.	2.	4.	8.	100.
1	$[f_{f,I}]_{+1}$	2	+1	+1.0187	+1.0378	+1.0763	+1.1586	+23.4690
		2.18	+1	+1.0941	+1.1738	+1.3102	+1.5454	+23.8110
2	$[f_{g,I}]_{+1}$	2	+0.0451	+0.0411	+0.0361	+0.0235	-0.0103	+1
		2.18	+0.0435	+0.0686	+0.0860	+0.1091	+0.1366	+1
3	$[f_{f,II-III}]_{+1}$	2	0	-0.0153	-0.0310	-0.0636	-0.1318	-17.5183
		2.18	0	-0.0730	-0.1296	-0.2166	-0.3473	-16.0365
4	$[f_{g,II-III}]_{+1}$	2	+0.9761	+1.0038	+1.0811	+1.0848	+1.1911	0
		2.18	+0.8254	+0.7241	+0.6514	+0.5542	+0.4501	0
5	$[f_{f,III}]_{+1}$	2	0	-0.0153	-0.0310	-0.0636	-0.1318	-5.5221
		2.18	0	+0.0202	+0.0349	+0.0547	+0.0753	-4.3821
6	$[f_{g,III}]_{+1}$	2	+0.0106	+0.0054	-0.0008	-0.0158	-0.0548	0
		2.18	+0.0080	+0.0305	+0.0456	+0.0646	+0.0848	0
7	$[q_I]_{+1}$	2	+1	+1.0292	+1.0581	+1.1150	+1.2277	+1
		2.18	+1	+0.8818	+0.7972	+0.6849	+0.6145	+1
8	$[q_{II-III}]_{+1}$	2	0	-0.0048	-0.0106	-0.0249	-0.0627	0
		2.18	0	+0.0253	+0.0420	+0.0626	+0.0831	0
9	$10^{-6}E$	2	30	29.275	28.564	27.201	24.654	1.194
		2.18	30	27.767	26.070	23.529	20.032	1.194
10	m	2	3.3333	3.208	3.097	2.910	2.642	2
		2.18	3.3333	3.423	4.488	3.570	3.625	2.18

cementite are much the same, this Table is valid in general for a ferrous matrix. Since the value of m for cast iron frequently approaches 4, and the maximum value, occurring with $m_g = 2.18$ and 8% of graphite (to the nearest whole number), is still only 3.625, a "cross-section" is calculated and shown in Table VII. for

TABLE VII.—*Principal Load Factors per Unit Area and Bulk Elastic Constants in Ferrous Matrix with 8% of Lamellar Graphite, Modified by Varying Poisson's Ratio of Graphite.*

Row.	Principal Load Factors and Bulk Elastic Constants.	m_g .					
		2.	2.05.	2.1.	2.18.	2.4.	3.0.
1	$[f, f]_{+1}$	+1.1586	+1.3591	+1.4572	+1.5454	+1.6484	+1.7284
2	$[g, g]_{+1}$	-0.0103	+0.0996	+0.1285	+0.1366	+0.1256	+0.0981
3	$[f, (II-III)]_{+1}$	-0.1318	-0.2774	-0.3235	-0.3473	-0.3529	-0.3372
4	$[g, (II-III)]_{+1}$	+1.1911	+0.7923	+0.6076	+0.4501	+0.2705	+0.1321
5	$[f, (III-IV)]_{+1}$	-0.1318	-0.0344	+0.0209	+0.0753	+0.1470	+0.2090
6	$[g, (III-IV)]_{+1}$	-0.0548	+0.0512	+0.0782	+0.0848	+0.0702	+0.0391
7	$[g, I]_{+1}$	+1.2277	+0.8690	+0.7050	+0.6145	+0.4184	+0.3023
8	$[g, (II-III)]_{+1}$	-0.0627	+0.0425	+0.0722	+0.0831	+0.0785	+0.0584
9	$10^{-4}E$	24.654	22.114	20.99	20.032	18.979	18.202
10	m	2.642	2.982	3.263	3.625	4.197	5.040

8% of graphite, taking standard values of m_f , E_f and E_g , but values of m_g varying from 2 to 4. It is noticed that the bulk value of m exceeds 4 if m_g is greater than 2.3.

Soft commercial cast iron with not more than 3% of coarse lamellar graphite exhibits very small values of E and correspondingly large values of m ; furthermore, the yield resistance of graphite and the strength of its bond with the ferrous matrix are very small; finally, tessellated stresses due to cooling subject the graphite lamellæ to more or less initial compression of a three-dimensional character that imparts to its bond with the metallic matrix an apparent increase by the same amount. With these points in mind, a study of Tables VI. and VII. discloses the following process of stress and strain in cast iron due to increasing external force :

(a) It behaves under small loads like a cohesive structural compound of imperfect elasticity, since the graphite lamellæ have been pre-strained just up to the yield resistance of graphite by tessellated stresses due to cooling. The yield of graphite causes conditions to develop which to some extent subject "oblique lamellæ" of ferrite to bending besides tension, compression and shear.

(b) Above a certain external load per unit area, the bond between the graphite and the metallic matrix commences to break up sporadically. This process rapidly spreads with further increase of load, so that obliquely laminated slabs become strained under but a small share of the average stress f , owing to the mere bending of the ferrite lamellæ, and slabs with

lamellæ at right angles to the force do not carry any load at all. Under great external stress the load is carried exclusively by ferrite lamellæ which are parallel or almost parallel to the external stress, *i.e.*, by "longitudinal" ferrite lamellæ the load factor per unit area of which is given by $[f_{f,l}]_{+1}$.

The above considerations suggest how to find approximate values for the actual load factors per unit area in cast iron due to the application of external forces. For a prismatic test specimen determine the stress-strain curve and the lateral strain with a gradually increasing axial load. For any value of the external stress in question find the slope of the local tangents to both the stress/longitudinal-strain and stress/lateral-strain curves and calculate the true moduli of direct and lateral strain. Then use equations (14) with standard values of m_f , E_f and E_g and put in arbitrary values of m_g and u_1 (which may be quite different from that of the actual cast iron used) until the solution of the equations gives the same values of s and m as were obtained by experiment. Knowledge of the value of the principal load factor $[f_{f,l}]_{+1}$ which corresponds to this theoretically comparable cast iron of perfect elasticity and cohesion makes an approximate quantitative reconstruction of the actual load distribution in the given cast iron readily possible, even without knowing the correct value of Poisson's ratio for graphite.

The lamellæ of graphite in cast iron are in general twisted in a complex manner, and the ferrous matrix is intersected more or less irregularly. The results obtained from equations (14) to (16) are, nevertheless, quite correct if applied to portions of either of the structural components the orientation of which is in accordance with that of the "correctly laminated" slab of the theory.

Rows 1 to 9 of Table VIII., calculated with equations (17), account for the theoretical load distribution in blackheart malleable cast iron. Since, owing to tessellated cooling stresses, graphite is subjected to more or less "uniform" hydrostatic compression, possibly much reduced below the values of Table V. by the plastic yield of the matrix, the bond between the graphite and the matrix attains a considerably increased apparent value. Yield under small loads is of only moderate effect on the bulk properties, since it is restricted to small regions and does not involve bending in the matrix.

Whiteheart malleable cast iron may best be considered as a porous ferrous metal with cavities having the same volume fraction as the previous graphite content. Rows 10 to 14 of Table VIII. were calculated with equations (18); they contain some significant load factors per unit area which are also valid for porous iron produced by sintering. For both types of malleable cast iron the value of $[f_{a,o}]_{+1}$ plays the leading rôle, corresponding to that of $[f_{f,l}]_{+1}$ in Tables VI. and VII.

Considering that the graphite content of malleable cast iron is usually about 2%, it is noticed that the true elasticity of the metal

TABLE VIII.—Principal Load Factors per Unit Area and Bulk Elastic Constants with Pseudo-Spherical Graphite or Voids of Corresponding Volume Fraction in Ferrous Matrix due to Application of External Force.

Row.	Sys-tem.	Principal Load Factors and Bulk Elastic Constants.	m_g .	Graphite. Weight-%.					
				0.	1.	2.	4.	8.	100.
1	With pseudo-spherical graphite.	$[p_j]_{+1}$	2	+0.1538	+0.2229	+0.2504	+0.2814	+0.3090	0
			2.18	+0.0367	+0.0537	+0.0618	+0.0734	+0.0903	0
2		$[p_s]_{+1}$	2	0	+0.0616	+0.0892	+0.1240	+0.1623	0
			2.18	0	+0.0351	+0.0492	+0.0668	+0.0879	0
3		$[f_{a,i}]_{+1}$	2	+0.1936	+0.2651	+0.2943	+0.3285	+0.3625	+1
			2.18	+0.0735	+0.0925	+0.1024	+0.1175	+0.1415	+1
4		$[f_{a,o}]_{+1}$	2	+1	+1.0864	+1.1387	+1.2272	+1.3887	+23.4690
			2.18	+1	+1.1066	+1.1764	+1.2986	+1.5234	+23.8110
5		$[p]_{+1}$	2	0	-0.0296	-0.0608	-0.1254	-0.2597	-17.5183
			2.18	0	-0.0168	-0.0335	-0.0676	-0.1407	-16.0365
6		$[f_{t,o}]_{+1}$	2	-0.1538	-0.1376	-0.1354	-0.1398	-0.1632	-5.5221
			2.18	-0.0367	+0.0121	+0.0314	+0.0658	+0.0825	-4.3822
7		$[f_{t,o}]_{+1}$	2	0	+0.0237	+0.0268	+0.0176	+0.0165	-5.5221
			2.18	0	+0.0307	+0.0442	+0.0613	+0.0849	-4.3822
8		$10^{-4}E$	2	30	29.078	28.198	26.542	23.581	1.194
			2.18	30	28.985	27.980	26.068	22.681	1.194
9		m	2	3.3333	3.217	3.106	2.915	2.640	2
			2.18	3.3333	3.319	3.315	3.314	3.319	2.18
10	With pseudo-spherical voids.	Volume fraction of voids, b^3 .		0	0.0341	0.0666	0.1271	0.2331	1
11		$[f_{a,o}]_{+1} = \frac{1}{1-b^3}$		+1	+1.1175	+1.1966	+1.3384	+1.6360	+ ∞
12		$[p_s]_{+1}$		0	+0.0277	+0.0376	+0.0487	+0.0602	+0.0882
13		$10^{-4}E$		30	28.916	27.833	25.748	22.032	0
14		m		3.3333	3.354	3.390	3.484	3.706	7.6667 (= $2m_f$ + 1)

is distinctly "softer" than the elastic theory indicates in Table VIII. It is, therefore, advisable once more to resort to the determination of the principal load factor $[f_{a,o}]_{+1}$ of a theoretically comparable malleable iron of perfect elasticity and cohesion. Table IX., calculated for blackheart malleable iron again containing 8%

TABLE IX.—Principal Load Factors per Unit Area and Bulk Elastic Constants in Ferrous Matrix with 8% of Pseudo-Spherical Graphite, Modified by Varying Poisson's Ratio of Graphite.

Row.	Principal Load Factors and Bulk Elastic Constants.	m_g .						
		2.	2.05.	2.1.	2.18.	2.4.	3.0.	4.0.
1	$[p_j]_{+1}$	+0.3090	+0.1865	+0.1551	+0.0903	+0.0465	+0.0084	+0.0053
2	$[p_s]_{+1}$	+0.1623	+0.1206	+0.1101	+0.0879	+0.0729	+0.0596	+0.0585
3	$[f_{a,i}]_{+1}$	+0.3625	+0.2383	+0.2049	+0.1415	+0.0983	+0.0659	+0.0630
4	$[f_{a,o}]_{+1}$	+1.3887	+1.4644	+1.4848	+1.5234	+1.5497	+1.5695	+1.5712
5	$[p]_{+1}$	-0.2597	-0.1931	-0.1762	-0.1407	-0.1167	-0.0954	-0.0936
6	$[f_{t,o}]_{+1}$	-0.1632	-0.0255	+0.0101	+0.0825	+0.1315	+0.1731	+0.1766
7	$[f_{t,o}]_{+1}$	-0.0165	+0.0404	+0.0551	+0.0849	+0.1051	+0.1220	+0.1234
8	$10^{-4}E$	23.581	23.066	22.927	22.681	22.516	22.405	19.781
9	m	2.640	2.989	3.091	3.319	3.491	3.651	4.149

graphite with various values of m_g , thoroughly confirms the suitability of the method in this case also. It is noteworthy how with increasing m_g the value of $[f_{a,o}]_{+1}$ in row 4 of Table IX. approaches that of the whiteheart malleable iron with voids corresponding to the "removal" of 8% of graphite, as given in row 11 of Table VIII. This indicates that the method of elastic representation may work well also with mixed types of malleable iron.

The graphite lamellæ of high-tensile-strength cast iron may be considered as more or less degenerated in the direction of a compacted shape. The process of straining must be modified along similar lines, *i.e.*, more or less towards the feature of the malleable iron. It may be worth while to investigate how far the values of the significant load factors per unit area—*i.e.*, $[f_{f,l}]_{+1}$ of Tables VI. and VII., and $[f_{a,o}]_{+1}$ of Tables VIII. and IX.—compare for the same set of values of the constants of elasticity, E and m , of the bulk.

Owing to the effect of the actual breaking-up of the bond between the graphite and matrix, it is obvious that the behaviour, especially of cast iron, is different, in general, when compression is applied instead of tension, as has been pointed out repeatedly in the past. The detrimental effect on both load-carrying capacity and ductility of the stress-concentration set up by the voids previously occupied by graphite has also been carefully discussed. The investigation of the tessellated stresses represents another contribution to the analysis of the micro-mechanics of cast and malleable iron.

PHASE TRANSFORMATION.

Let the old and new phases be considered to have the same elastic constants. It is then recognised from equation (21) that during the first half of the process of transformation, *i.e.*, from $X = 0$ to $X = 0.5$, where X denotes the volume fraction of the new phase, external energy is required for the process of tessellation. The maximum strain energy and the quantity of external energy required are observed with $X = 0.5$ at half transformation, and amount to $U_{\max.} = \frac{1}{4} \cdot \frac{mE}{m-1} \lambda^2$. For the process of transformation

of austenite to α -martensite near room temperature, $\lambda = 0.01137$ and $U_{\max.} = 1385$ in.lb. per cu. in., a hypothetical figure since yield and redistribution of stresses have not been considered. Over the second half of the transformation, *i.e.*, for $X = 0.5$ towards $X = 1$, strain energy is released gradually and is expended on the acceleration of the process of transformation and in generating vibrations.

While equation (21) is that of a parabola with $U = 0$ both before the beginning of and after completion of the transformation and with an apex at $X = 0.5$, the energy curve obtained with phases of different elastic constants is of a shape different from a parabola, with an apex not at $X = 0.5$, but the nature of the process is the same in principle.

The character of the strain energy which may develop with phase transformation due to tessellated stresses in the enveloping surface layer of the grains of the new phase is the same in general. Energy is furthermore required for the modification of the position of the atoms from that in the old to that in the new phase. The strain energy stored in nuclei due to cooling down or heating up to the temperature of phase transformation can, in general, be neglected as a possible source of external energy. The energy has to be provided by the difference between the free energies of the old and the new phases. Consequently, the following wording may be suggested for the free-energy phase rule :

At any temperature, that phase is theoretically stable which has least free energy ; whether, at a certain temperature, the unstable phase changes to the stable one or not and the degree of transformation depend on the actual balance of the transformation potentials on the one hand, and the necessary force to start and energy to carry out the transformation on the other. It cannot be expected, in general, that transformation would ever take place at the exact temperature at which the free energies of the two phases are equal without undercooling or overheating occurring.

Plastic yield during phase transformation does not, in principle, affect the above reasoning. The same holds for the transformation taking place at elevated temperatures, with U reduced owing to the decrease of the factor $\frac{mE}{m-1}$ and of the yield resistance of the material.

FATIGUE.

Let us consider more or less ductile materials, built up, for simplicity's sake, of components having the same elastic constants, the compound body exhibiting fairly perfect elasticity within certain limits of the simple stress applied. Let the material furthermore be supposed to be primarily subjected to tessellated stresses of considerable magnitude due to cooling. All of these conditions are realised with normalised or spheroidised steel. The conventional figure of the apparent limit of elasticity, when determined in simple tension, is only part of the true stress actually withstood, the latter being the sum of the apparent limit of elasticity and the maximum reduced stress f_{red} due to the combination of tessellated stresses of structural type and those due to crystal anisotropy. Regardless of the possibilities of some other process, as, for instance, precipitation-hardening, contributing considerably to this phenomenon, let it be called in a cumulative sense super-elasticity.

Damping in alternating strain is one of the first indications of the combined effect of external and internal stresses having exceeded the limit of elasticity. Remembering the singular feature of the

presence of intersected units of tessellation in the free surface, the question may be asked whether initial damping develops exclusively in such units of the surface layer, since they might have been more or less deprived of their capacity to exhibit super-elasticity. If it is so, intersected surface units are at first selectively subjected to small alternating plastic strains, but as the external alternating stress increases in magnitude the intact internal units are also plastically strained, but always to a considerably less extent than the surface units. This would readily explain the general tendency of fatigue cracks to start in the surface layer, *i.e.*, the surface deficiency. To study this question further, it would be interesting to investigate the magnitude of initial damping in alternating tension-compression with homogeneous specimens free from body stresses, having the same cross-sectional area but a varying ratio of perimeter to area.

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PRESENT POSITION OF THE CORROSION COMMITTEE'S FIELD TESTS ON ATMOSPHERIC CORROSION (UNPAINTED SPECIMENS).¹

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(Figs. 1 and 2 = Plates X. and XI.)

Paper No. 10/1943 of the Corrosion Committee.

SUMMARY.

This paper brings up to date the information given in earlier Reports of the Corrosion Committee concerning atmospheric corrosion tests made on ordinary ferrous materials of construction, including wrought irons, ingot irons and steels both of ordinary and of the low-alloy type. The main tests were made at fourteen stations, seven at home and seven overseas, representing marine, rural, industrial, tropical and arctic conditions. The specimens measured $15 \times 10 \times \frac{3}{8}$ in., and were exposed vertically.

Comparison of the corrosive effects of different atmospheres indicates that the primary cause of serious corrosion of ferrous materials is pollution of the air with sulphur gases. The maximum rate of corrosion observed for ordinary mild steel over a five years' period was 0.0042 in. per year in the industrial atmosphere of Sheffield. Much lower rates were recorded at most overseas stations. The corrosion rate probably decreases with increasing time of exposure.

Wrought irons containing much slag are more resistant to atmospheric corrosion than mild steel, but those with low slag contents are more corrodible. Ingot iron resists general corrosion to much the same extent as mild steel, but Aston-Byers iron (made by mixing a synthetic slag with a heat of dead-mild steel) is slightly more corrodible.

Concerning low-percentage alloy additions, copper is beneficial when the steel is exposed in the open air, but not in enclosed atmospheres (railway tunnels, &c.). Chromium, silicon, nickel and probably arsenic all improve the corrosion resistance.

In general, the surface condition in which the specimens are exposed has little influence on the relative results for different materials, except that in the case of certain wrought irons with mill scales that are particularly resistant to weathering, abnormal results may be obtained for specimens exposed in the as-rolled condition, owing to the accumulation of rust between the scale and the metal which leads to local corrosion. Machined surfaces corrode more than sand-blasted ones.

To ensure complete scale removal, by weathering, from $\frac{3}{8}$ -in. plates of ordinary mild steel, exposure for about one year is necessary in Britain; under the milder conditions overseas descaling may

¹ Received March 2, 1943. This paper is published by authority of the Corrosion Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

be incomplete after five years' exposure. Copper in the steel does not affect the descaling period.

The method of piling employed in making wrought irons has little effect on their resistance to corrosion, except that rerolling the puddled bars causes a marked improvement, which may be attributed to the consolidation of the surface. Further reworking has little effect.

The rate of atmospheric corrosion varies with the height above ground-level, but is also governed by local conditions. Horizontal surfaces corrode more than vertical ones, probably because rain water lingers on them and they remain wet longer.

Hot-galvanised mild-steel specimens exposed in a rural atmosphere in Wales showed little sign of deterioration of the zinc coating after eleven years. The probable lives of galvanised coatings are calculated on the basis of test results obtained on zinc specimens exposed at the corrosion stations. For equivalent corrosion resistance there is a marked difference between the gauges of galvanised and black plates; the latter need to be appreciably thicker.

1.—INTRODUCTION.

(a) *Experimental Details.*

THE present paper brings up to date the results of the main corrosion tests on specimens of various irons and steels exposed to the atmosphere in the bare condition that the author is conducting on behalf of the Corrosion Committee. Earlier reports on this long-range investigation will be found in the Committee's Reports.¹

It may be recalled that the programme has involved tests at fourteen exposure stations, seven at home and seven overseas (Table I.), and that the materials tested include mild steel, various types of wrought iron, ingot iron, Aston-Byers iron and various low-alloy steels (Table II.). All the materials are commercial products; in the great majority of cases their production was witnessed, and full details of the procedure followed, analyses, mechanical properties, &c., have been recorded. The standard size of specimen is $15 \times 10 \times \frac{3}{8}$ in.,² either rolled as flats or cut from plates. The surface condition before exposure was varied, as indicated in Table III. All specimens were weighed before test.

The specimens, in two horizontal rows of three (or, in a few cases, four), hang vertically on steel stands, freely exposed to the air (Fig. 1). Duplicates of each material are placed in different rows, to minimise any effect due to the different height from the ground.

The standard exposure period is five years, but in some cases, notably at Sheffield and Llanwrtyd Wells, one- and two-year tests have been made on similar sets of materials, and two additional

¹ First Report of the Corrosion Committee, *Iron and Steel Institute*, 1931, *Special Report No. 1*, p. 63. Second Report, 1934, *Special Report No. 5*, p. 17. Third Report, 1935, *Special Report No. 8*, p. 5. Fourth Report, 1936, *Special Report No. 13*, p. 21. Fifth Report, 1938, *Special Report No. 21*, p. 13.

² In a few cases the thickness varied from $\frac{3}{8}$ in.

TABLE I.—Particulars of the Corrosion Stations.

Home.					Overseas.						
Station.	Type of Atmosphere.	Mean Annual Temp. ° F.	Rainfall. In.	Relative Humidity. %.	Station.	Type of Atmosphere.	Position.		Temp. ° F.	Rainfall. In.	Relative Humidity. %.
							Lat. °.	Long. °.			
Calshot	Marine	51	26	84	Abisko, Sweden	Sub-polar	68 N.	19 E.	30	11	74
Dove Holes Tunnel	Railway tunnel	Apapa, Nigeria	Marine-tropical	7 N.	4 E.	80	72	79
Llanwrtyd Wells	Rural	47	55	79	Aro, Nigeria	Inland-tropical	7 N.	3 E.	77	45	84
Motherwell	Industrial	48	32	82	Basrah	Dry sub-tropical	31 N.	48 E.	75	7	64
Redcar	Marine-industrial	48	25	84	Congella, South Africa	Marine	30 S.	31 E.	71	43	76
Sheffield	Industrial	48	30	84	Khartoum	Dry tropical	16 N.	33 E.	85	6	31
Woolwich	Industrial	50	23	81	Singapore	Marine-tropical	2 N.	104 E.	81	95	80

TABLE II.—Particulars of the Materials Tested.

Designation.	Analysis.						Mechanical Properties. ¹		
	C. %.	Cr. %.	Cu. %.	Mn. %.	P. %.	Si. %.	Yield Point. Tons per sq. in.	Max. Stress. Tons per sq. in.	Elongation on 2 in. %
<i>Steels.</i> ²									
K.	0.25	0.98	0.03	0.60	0.04	0.12	25	39	27.8
L.	0.25	0.59	0.48	0.58	0.03	0.13	24	37	29.5
M.	0.27	0.60	0.50	0.89	0.04	0.15	27	41	25.0
N.	0.26	0.95	0.48	0.84	0.05	0.13	31	46	20.5
O.	0.23	0.03	0.52	1.56	0.04	0.33	29	43	23.5
P ³ .	0.17	...	0.05	0.55	0.04	0.06
Q ⁴ .	0.14	...	0.10	0.56	0.04	0.09
W ⁵ .	0.03	Nil	0.04	0.03	0.01	0.03	12	21	41.8
X.	0.20	Nil	0.02	0.59	0.04	0.02	18	30	31.7
X ² .	0.24	0.04	0.02	0.57	0.04	0.02	18	30	33.8
XK.	0.21	0.07	0.03	0.59	0.04	0.10	20	31	30.8
Y.	0.21	Nil	0.22	0.59	0.04	0.03	19	31	32.3
Z.	0.21	Nil	0.48	0.61	0.04	0.03	18	32	29.1
ZK.	0.23	0.05	0.50	0.60	0.03	0.12	21	33	32.3
<i>Wrought Irons.</i>									
H Aston-Byers	0.02	Trace	Trace	0.02	0.14	0.13	13	18	13.3
R Swedish	0.03	Nil	Trace	Nil	0.05	0.02	13	20	29.3
S Swedish	0.03	Nil	0.60	Nil	0.05	0.02	15	22	26.3
T Staffordshire	0.03	Trace	0.04	0.02	0.24	0.14	15	22	17.0
T ² Staffordshire ⁶	0.02	0.01	0.07	0.01	0.32	0.13	16	21	12.4
V Scottish	0.03	Nil	0.12	0.03	0.17	0.16	15	21	14.6

¹ Mean values for transverse and longitudinal tests.² Particulars of other steels from the Institute of Welding, &c., tested in one series only are given in Table XIII.³ 0.13% As, 0.05% S. ⁴ 0.12% As, 0.04% S. ⁵ Ingot iron. ⁶ A "repeat" batch of wrought iron T.

sets will be exposed for longer periods (ten years and more), to determine how the rate of corrosion varies with time. A few tests over shorter periods have been made for other purposes.

All specimens are inspected at intervals, the chief observations being the extent to which the mill scale has been shed from as-rolled specimens and the colour and type of the rust on the various materials.

After exposure, the specimens are examined and weighed, both as received in the laboratory and after removal of the rust, which is

TABLE III.—*Particulars of Surface Treatments before Exposure.*¹

With Mill Scale.	Without Mill Scale.
r. <i>As-rolled</i> .—Materials prepared by the normal hot-rolling process, kept as free from rust as possible, and cleaned with carbon tetrachloride before exposure.	p. <i>Pickled</i> .—In 15% by volume sulphuric acid at about 40° C. Approximate time required 50 min.
r1. <i>As-rolled, reduced rolling temperature</i> .—As (r), but rolling completed at a reduced rolling temperature. With some materials (<i>cf.</i> Third Report, <i>loc. cit.</i> , p. 68) different methods of obtaining a low-temperature finish were compared.	s. <i>Sand-blasted</i> . ² —Air pressure 12 lb. per sq. in.; distance from nozzle 3-6 in. Leighton Buzzard sand.
r2. <i>As-rolled, alternative rolling temperature</i> .—As (r), but rolling not conducted normally, the material usually being finished at a higher temperature than normal.	m. <i>Machined</i> .—Depth of cut $\frac{1}{16}$ in.; traverse $\frac{1}{4}$ in.; cutting speed 60 ft. per min.; done dry.
	pol. <i>Polished</i> .—Buffed to a mirror finish in 7 stages: (1) Ground on stone, (2) 60-grade emery, (3) 90-grade emery, (4) 140-grade emery, (5) emery compo, (6) Tripoli compo, (7) Chromic compo. Peripheral speed of wheel about 6000 ft. per min. for stages (1) and (2) and 7500 ft. per min. for finishing stages.

¹ For further details see First Report, *loc. cit.*, p. 67.

² Sand-blasting was used for the earliest series of tests, as described. In later series shot-blasting has been substituted. The two processes may be regarded as equivalent for the present purpose.

effected in two stages. First the specimens are wire-brushed to remove loose rust and mill scale, if present; then the rust still remaining in the pores of the surface is removed by immersion in a bath of warm dilute sulphuric acid containing an inhibitor (*see* Appendix A). From the final weighing the loss in weight is determined, minor corrections being applied for slight differences in surface area.

Since, with a few exceptions mentioned later, no marked pitting has been observed in these tests, the losses in weight may be taken

as a true index of the relative resistance to corrosion of the various materials.

(b) *Nature of the Results.*

A total of 1054 specimens has been exposed during the course of this research. Tests have now been completed on 856, including 18 specimens at Singapore which presumably must be regarded as lost.

The results given are means of two specimens; in the great majority of cases the duplicates agreed within 5% (*e.g.*, 97 g. and 102 g.). Where applicable the rate of corrosion is expressed in thousandths of an inch (mils) of metal per year, *i.e.*, the thickness of the layer of metal destroyed by rusting in the course of a year. This figure is readily calculated from the observed loss in weight by means of a simple factor, as described in Appendix A.

Comparisons of dissimilar materials are made by reference to the standard reference material, ordinary low-copper mild steel X, which was included in all test series; the relative corrosion of this steel is taken as 100.

The data thus accumulated permit of authoritative answers to the following questions :

(i) What is the effect of different types of atmosphere on the rate of rusting of ordinary mild steel? (*See Section 2*).

(ii) What is this rate, and how does it vary with the duration of exposure? (*See Section 3*).

(iii) To what extent does the resistance of mild steel to atmospheric corrosion differ from that of wrought iron or ingot iron? (*See Section 4*).

(iv) What is the effect of the addition of low percentages of alloying elements on the rate of atmospheric corrosion of mild steel? (*See Section 5*).

(v) What is the effect, if any, of the initial surface condition? (*See Section 6*).

(vi) What length of exposure is needed to remove the mill scale from as-rolled iron or steel by natural weathering? (*See Section 7*).

(vii) What are the effects of sundry variables (the method of piling wrought iron; different conditions of test exposure)? (*See Section 8*).

(viii) What protection is afforded to steel by galvanised coatings? (*See Section 9*).

(c) *Acknowledgments.*

The author wishes to record his appreciation and thanks to the Chairman, Dr. W. H. Hatfield, F.R.S., the Vice-Chairman, Dr. T. Swinden, and the Members of the Corrosion Committee for

the encouragement and assistance which they have given him in the conduct of this work on their behalf. His colleague, Dr. T. A. Banfield, has collaborated helpfully in the routine inspections, preparation and final examination of the specimens; more recently Mr. H. A. Holden has also done so.

Most of the Government departments, scientific institutions and individual companies referred to in the Corrosion Committee's Fifth Report have continued to support the investigation in the various ways described. The Committee desire the author to express here their cordial thanks to those concerned for this assistance, sometimes rendered under difficult circumstances.

2.—EFFECT OF CLIMATE ON THE RATE OF ATMOSPHERIC CORROSION.

Rates of Corrosion of Mild Steel over a Five-Year Period.

The effect of different climates on the rate of atmospheric corrosion of ordinary irons and steels is best illustrated by the data summarised in Table IV. These are the figures in mils per year calculated from the observed losses in weight of specimens of the standard reference steel, mild steel X, containing 0.2% of carbon, 0.6% of manganese and no added copper (actually 0.02%). Values are available for all fourteen corrosion stations, in some cases for two or even three series of tests. The reproducibility from one test series to another at the same station is good.

The specimens concerned were exposed with the mill scale. At the stations where corrosion is appreciable this mill scale was shed in its entirety, and, as will be shown later in Section 6, the calculated corrosion rate, as compared with that for similar steel from which the mill scale had been removed before exposure, was not markedly affected thereby. This applies to all the home stations. On the other hand, at those overseas stations, such as Khartoum and Abisko, where the rate of corrosion was small, the mill scale was incompletely removed during exposure and its presence on the steel interferes with the accuracy of the calculation. For practical purposes this is unimportant, since the rate of corrosion is so low as to have little practical significance. Roughly, the dividing line between complete and incomplete mill scale removal lies at 0.5 mil per year.

The results may conveniently be compared by expressing them all in terms of the average rate, 4.21 mils per year, observed in the three series of tests at Sheffield. The exposure station at Sheffield is situated in the heart of the industrial district and the atmosphere there is very corrosive. By this standard the corrosion rates at other home stations are low, whilst, with the exception of Congella, South Africa, where there is distinct industrial activity, those at overseas stations are slight.

TABLE IV.—*Rate of Corrosion of Mild Steel over a 5-Year Period.*

Specimens exposed with mill scale.

Home.				Overseas.			
Station.	Test Series.	Mils per Year.	Relative to Sheffield (= 100).	Station.	Test Series.	Mils per Year.	Relative to Sheffield (= 100).
Calshot	I. & II.	1.62	38	Abisko ¹	I. & II.	0.27	6
Dove Holes Tunnel	I.	2.39	57	Apapa	I.	0.77	18
	II.	2.29	54	Aro	I.	0.45	11
Llanwrtyd Wells.	I.	1.22	29	Basrah	I.	0.46	11
	II.	1.26	30	Congella	I.	1.82	43
Motherwell	I.	2.15	51		III.	1.85	44
Redcar	I.	1.92	46	Khartoum	I.	0.03 ²	1
Sheffield	I. & II.	4.30	102	Singapore ¹ .	II.	0.03 ²	1
	III.	4.36	104		I.	0.62	15
	IV.	3.96	94		II.	0.53	13
Woolwich	I.	2.26	54				

¹ Owing to the outbreak of war, it was decided to continue the exposure of test series III. at Abisko and Singapore beyond 5 years. The Singapore specimens have since been presumed lost.

² 80% of the mill scale was intact after exposure.



FIG. 1.—Method of Exposing Specimens.
(Reproduced, by courtesy, from the author's book "The Corrosion of Iron and Steel." London, 1940 : Messrs. Chapman and Hall, Ltd.)

[Hudson.]

[To face p. 168 P.]



FIG. 2.—Corroded Stands at Congella, South Africa. The angles are $2 \times 2 \times \frac{1}{4}$ in. steel.

The second most corrosive atmosphere is that of the Dove Holes Tunnel, where the corrosion rate was 57% of that at Sheffield. The conditions here were peculiar, in that the specimens were exposed in man-holes inside the tunnel, which is $1\frac{3}{4}$ miles long, very humid and, at the particular spot selected for the test, free from smoke at only comparatively infrequent intervals. There is no rainfall to remove rust; consequently the specimens become covered with a thick wet skin built up from rust and mechanically entangled soot, which never dries. These conditions of exposure fall outside the range of those encountered at the other thirteen stations, where the specimens were freely suspended in the open air, and, as will be seen later, lead to anomalous results.

The remaining industrial atmospheres, Motherwell, Redcar and Woolwich, are only half as corrosive as Sheffield. Here, although the atmospheres are correctly described as "industrial," the actual sites were situated on the fringe of the industrial activity, rather than in its centre, in a zone where, as is frequently the case, there is a rapid transition from industrial plant to open country.

Corrosion in the marine atmosphere of Calshot was less than 40% of that at Sheffield. Since the specimens were exposed at the edge of the spit and were exposed at times to salt spray, it may be concluded that, although proximity to the sea may lead to severe corrosion in certain cases, in general sea salts are not so corrosive as the markedly acid conditions which result from severe industrial pollution of the atmosphere, chiefly by sulphur compounds.

The rate at the rural station Llanwrtyd Wells was barely 30% of that at Sheffield. It is probable that in most rural districts even lower rates would be observed, because analysis of the rain water at Llanwrtyd Wells revealed the presence in it of considerable quantities of chlorides, no doubt derived from wind-borne spray carried in from the water of Cardigan Bay.

The significance of the results for the overseas stations, where, with the exception of Congella, the rate of corrosion was less than one-fifth of that at Sheffield, may be illustrated by the following calculations. If the test specimens were only $\frac{1}{8}$ in. thick and the same rates of corrosion (on both sides) continued they would be completely destroyed after 15 years' exposure at Sheffield. At Khartoum, on the other hand, approximately 1400 years would be needed; at Abisko, within the polar circle, some 250 years; in Nigeria, at Apapa and Aro, about 80 or 140 years; at Basrah 140 years; and at Singapore 110 years.

It may be concluded from the above that, as a rule, straightforward corrosion of iron and steel should not be marked in non-industrial, tropical or sub-polar climates and that the primary cause of severe corrosion is industrial pollution. Unfortunately this conclusion is not so reassuring as it sounds, for two reasons: (a) The fact that iron or steel is used at all at the place concerned will often imply that there is at least some industrial activity there,

and (b) corrosion may not be straightforward. The first point is obvious; it may be profitable to examine the second.

Apart from perforation by pitting, which is not common in atmospheric corrosion although of frequent occurrence where corrosion by liquids is concerned, the worst type of atmospheric corrosion is that which results in the formation of a thick scale-like layer of rust which remains in contact with the metal. Such scale formation sometimes occurs on steel having members in contact with wood, *e.g.*, the planks of a ship's deck; it may also be seen on the webs of some rails. The primary cause of this phenomenon seems to be either that the part concerned is sheltered, as in the cases cited, so that rust removal by natural causes such as rain is hindered, or that for some reason the rust is held in contact with the steel in the early stages, after which a thick adherent layer is built up gradually. Examples of the latter cause are given by certain as-rolled specimens at Calshot and Sheffield, where, as discussed later, the mill scale was not shed but was undermined by rust, so that after five years' exposure there were local areas where the rust was fully $\frac{1}{8}$ in. thick and capped on the outside by the original unchanged mill scale.¹ A paint film may serve the same purpose if, when failure begins, the rust develops between the as-yet intact parts of the film and the metal itself. This may be illustrated by the photograph reproduced in Fig. 2, which shows part of two of the corrosion stands at Congella; owing to a misunderstanding repainting had been deferred for an unduly long period. Some of the $2 \times 2 \times \frac{1}{4}$ -in. angles of these stands were literally corroded through.

Metallurgical examination of badly corroded and lightly corroded members failed to show any characteristic of the steel used for the former that would account for their excessive corrosion. The explanation, in this and similar cases, is that the thick local layers of rust retain moisture in contact with the specimen, leading to rapid corrosion beneath them, partly, no doubt, as a result of differential aeration. This action is obviously much facilitated when electrolytes are present, and for this purpose saline spray derived from sea salts seems to be as effective as the acid rain water in industrial atmospheres, since corrosion of this type is frequently observed in marine atmospheres.

Hence, it may be concluded that :

(i) In certain climates, particularly where the relative humidity or the temperature is low, it may be unnecessary to protect steel at all, provided that there is no danger of local attack being promoted by the formation of scaly rust. This will largely depend on the form in which the steel is used and on local conditions; the best ultimate criterion will be experience gained from the behaviour of similar structures in the past. For instance, in certain parts of Nigeria it should be possible to use ordinary black

¹ See Section 4(a) (i).

corrugated sheets for roofing without protecting them against corrosion.¹ On the other hand, near the coast the presence of salt spray in the air may be found to produce the scaly-rust type of attack and painting may be necessary; this may even depend on the pitch of the roof.

(ii) Thick rust should never be allowed to accumulate on iron or steel. A thin uniform fine layer of rust may not be harmful, but rust of the scaly type is deadly.

3.—VARIATION IN THE RATE OF ATMOSPHERIC CORROSION OF MILD STEEL WITH TIME.

The next question to be discussed is how the rate of attack of the atmosphere on mild steel varies with increasing duration of exposure, or, in other words, how far can the rates of corrosion established by experiments over comparatively short periods of exposure be used to predict the effect of corrosion over longer ones? Three series of tests at Sheffield and a fourth made at Llanwrtyd Wells supply information on this point. In each case similar sets of specimens were exposed simultaneously and removed, respectively, after one, two and five years' exposure. The ordinary standard mild steel X was included in all sets and the corrosion rates observed for this material are given in Table V. The losses

TABLE V.—*Variation in Corrosion Rate of Mild Steel with Time.*

Specimens exposed with mill scale.

Station.	Test Series.	Loss in Weight, G. per Specimen.			Corrosion Rate, Mils per Year.		
		1 Year.	2 Years.	5 Years.	1 Year.	2 Years.	5 Years.
Llanwrtyd Wells	II.	150	189	260	3.63	2.29	1.26
Sheffield	I. & II.	214	359	889	5.18	4.35	4.30
	III.	229	420	900	5.54	5.08	4.36
	IV.	211	360	817	5.11	4.36	3.96

in weight of the specimens are plotted in Fig. 3, beneath which are shown the values for the losses in weight of ingot-iron pollution specimens (*cf.* Appendix B) which were exposed for periods of twelve months throughout the test periods. The latter are a rough index of annual variations in the corrosiveness of the atmosphere due to changing meteorological and industrial factors.

It is clear that at Llanwrtyd Wells there is a marked decrease in the rate of corrosion with time. At Sheffield this decrease, though evident, is less definite, particularly when it is borne in mind that the specimens were exposed with the mill scale, most of which is shed during the first year. In all four cases, the curves

¹ Temperature effects inside the building are another matter.

between one and five years' exposure are to all intents and purposes straight lines. Hence the following conclusion may be drawn :

In the absence of complicating factors, such as the formation of scaly rust, the corrosion of ordinary steel in the atmosphere is at worst directly proportional to the duration of exposure and may in practice prove less than this. Although the data presented here are limited to ordinary steel, this conclusion is broadly tenable, on the basis of the experimental results, for all other wrought irons or low-alloy steels tested.

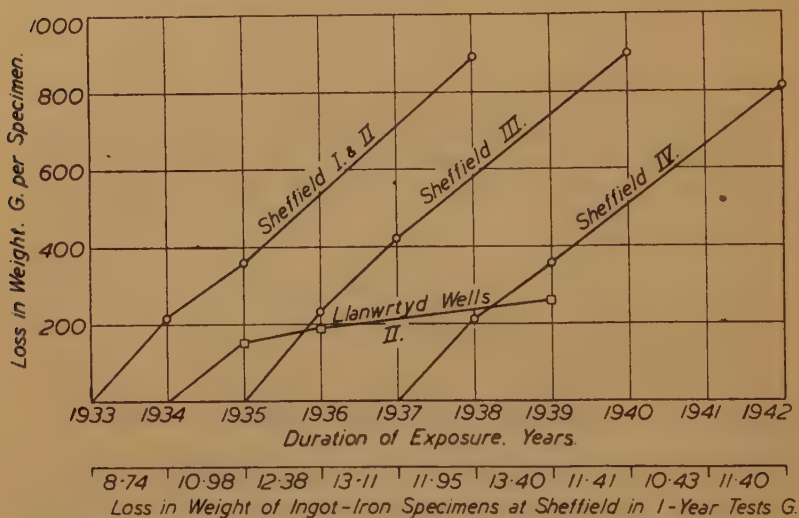


FIG. 3.—Variation in Corrosion of Mild Steel X with Time.

4.—COMPARATIVE RESISTANCE OF MILD STEEL, WROUGHT IRON, INGOT IRON AND ASTON-BYERS IRON TO ATMOSPHERIC CORROSION.

The findings deduced from the Committee's experiments as to the relative resistance to atmospheric corrosion of the ordinary ferrous structural materials, mild steel, wrought iron, &c., will now be considered. It should be made clear that this discussion is limited to materials free from any deliberate additions of alloying elements; low-alloy steels, &c. will be dealt with in the next Section.

(a) Wrought Iron.

The resistance of wrought iron to atmospheric corrosion in relation to that of mild steel is determined by the type of wrought iron concerned. There is a sharp distinction between the behaviour of wrought irons produced from relatively impure ores, with high

TABLE VI.—Comparison of Mild Steel, Copper-Bearing Steel, Wrought Iron and Ingot Iron. (Parts I. and II.)

Specimens exposed with mill scale.

Station.	Duration of Test, Years.	Corrosion Rate of Steel X (Cu 0.02%), Mils per year.	Relative Corrosion (Mild Steel X = 100).						
			Wrought Irons.			Ingot Iron W.	Mild Steels.		
			R Swedish.	S Swedish (Cu 0.6%).	T Staffordshire.		Y (Cu 0.2%).	Z (Cu 0.5%).	
Abisko	5	0.27	...	See footnote No. 1.	...	148	81	78	
Calshot	5	1.62	98	...	113	96	
Dove Holes Tunnel	5	2.29	...	92	78				
Khartoum	5	0.03	...	See footnote No. 1.	...				
Llanwrtyd Wells	1	3.63	...	77	...	89	66	70	
	2	2.29	111	83	88	93	72	74	
	5	1.26	111	89	78	110	84	84	
	1	5.18	...	82	...	88	78	77	
Sheffield	2	4.35	150	75	73	93	79	77	
	5	4.30	155	68	77	104	80	79	
Singapore	5	0.53	77 ²	101	

¹ The losses in weight of the specimens at Abisko and Khartoum were so small that no comparison of materials is warranted.² These specimens were incompletely descaled at the end of the test.

silicon and phosphorus contents, and those produced from high-grade ores of Swedish or other origin. In the tests under discussion, the former type was represented by a Staffordshire and a Scottish wrought iron (materials *T* and *V*, respectively, of Table II.), the latter by a Swedish Lancashire iron (material *R*). The essential difference between them lies in their slag content; as is reflected by the analyses for phosphorus and silicon shown in Table II., this is much higher in the British wrought irons than in the Swedish one.

The experimental fact, which is demonstrated by the results grouped in Tables VI. and VII., is that the less pure British wrought

TABLE VII.—*Comparison of Aston-Byers Iron, Wrought Iron, Mild Steel and Copper-Chromium Steel at Sheffield. (Part IV.)*

Duration of Test. Years.	Surface Condition.	Corrosion Rate of Steel X2. Mils per year.	Relative Corrosion.			
			Aston-Byers Iron <i>H</i> / <i>AB</i> .	Wrought Iron <i>T</i> 2.	Mild Steel X2.	Steel <i>N</i> (Cr 1.0%, Cu 0.5%).
1	Sand-blasted	4.53	114	75	100	62
1	} As-rolled {	5.11	99	67	100	70
2		4.36	103	64	100	...
5		3.96	103	64	100	40

irons have a superior corrosion resistance to that of ordinary mild steel, whereas the very pure Swedish iron is markedly inferior to the latter material. In round figures, taking the corrosion of mild steel as 100, the margins in favour of the British wrought irons, or to the disadvantage of the Swedish material, may both be assessed at 25%.

The superiority of the less pure wrought irons as compared with mild steel may be attributed to three factors :

(i) *Greater Resistance of the Mill Scale to Corrosion.*—It is a fact that the large quantities of slag present in irons of this type are liquid at the initial rolling temperature of the piles; they flow over the surface of the rolled material and form a crude enamel-like glaze on its surface. The resulting mill scale has a protective effect as compared with that on mild steel, ingot iron or the pure Swedish wrought iron. This effect is naturally most marked in the early stages of exposure and may be illustrated by the figures given in Table VIII. for the descaling and losses in weight of these materials after the first year's exposure at Llanwrtyd Wells and Sheffield. Two sets of data are given which refer, respectively, to the loss in weight on exposure, for which determination the specimens were weighed exactly as they had been removed (without any cleaning whatever), and to the loss in weight after scratch-brushing, in which case all loose rust and mill scale was removed from the exposed specimens by thorough treatment with a wire-brush; these figures

are distinct from those used to calculate the corrosion rates, which, it will be remembered, are determined after the specimens have been cleaned to a metallic finish in a dilute acid bath containing an inhibitor.

TABLE VIII.—*Descaling and Loss in Weight of Mild Steel, Wrought Iron and Ingot Iron after One Year's Exposure.*

Material.	Mill Scale still Adhering. % by area.		Loss in Weight. G.			
			On Exposure.		After Scratch-Brushing.	
	Llanwrtyd Wells.	Sheffield.	Llanwrtyd Wells.	Sheffield.	Llanwrtyd Wells.	Sheffield.
<i>R</i> Swedish wrought iron .	0	22	81	212	95	249
<i>T</i> Staffordshire wrought iron .	29	33	22	58	43	91
<i>V</i> Scottish wrought iron .	62	60	7	15	34	76
<i>W</i> Ingot iron .	0	0	60	104	73	122
<i>X</i> Mild steel .	0	0	69	148	82	159

It is clear from Table VIII. that the losses in weight on exposure of the British wrought irons, especially of the Scottish wrought iron *V*, were low in comparison with those of the other materials and that considerable mill scale was still adhering to them after exposure; some but not all of this mill scale was loose and was removed by the subsequent wire-brushing. Underneath the intact scale no corrosion had occurred.

It follows that the mill scale on British wrought irons will protect them to some extent against atmospheric corrosion in the early stages of exposure, but the practical significance of this fact should not be overrated, since under commercial conditions it is extremely improbable that any wrought-iron section would go into service with a perfectly intact mill scale. Moreover, this very protective property carries with it the corresponding danger that if the mill scale adheres locally for too long rust may commence to form beneath it and severe corrosion of the scaly-rust type may result. This has, in fact, been observed in the present experiments. Reference to Table VI. will show an apparently anomalous result where, at Calshot, the corrosion of Staffordshire wrought iron *T* was 113% of that of the standard mild steel *X*, and not less as is generally the case. On both the wrought-iron specimens 10–25% of the mill scale was still adhering to the front surfaces, which faced the sea, but this was heavily undermined with rust, which had lifted it from contact with the metal; at these places corrosion of the metal beneath was more pronounced than over the general surface. The

same effect was observed on the Scottish wrought iron *V* and the ingot iron *W*, but, since in these cases only one specimen of each pair had been appreciably affected, it was more obvious. The losses in weight of duplicate specimens after cleaning were 289 g. and 396 g. for wrought iron *V* and 394 g. and 597 g. for ingot iron *W*, the specimen with the scaly rust being more affected in each case.

The high relative rate of corrosion of Swedish wrought iron *R* at Sheffield, 155% of that of steel *X* (Table VI.), is also associated with the formation of scaly rust on the specimens. No instance has been observed in these tests in which this type of attack has occurred on mild steel, for, although films of scaly rust sometimes form on these specimens, they are readily removed during rainy weather and rust of the granular type remains. It is clear that, since the development of scaly rust is often initiated by the presence of adherent scale, the presence of a semi-protective scale on an iron or steel is of doubtful value.

TABLE IX.—*Comparison of Mild Steel, Wrought Iron and Ingot Iron at Sheffield. (Parts I. and II., 5 Years' Exposure.)*

Material.	Initial Surface Condition.				
	As-Rolled.	Pickled.	Sand-Blasted.	Machined.	Polished.
	<i>Loss in Weight. G. per specimen.</i>				
X Mild steel	889	886	872	877	872
	<i>Relative Corrosion (steel X = 100).</i>				
R Swedish wrought iron	155	135	132	135	123
T Staffordshire wrought iron	77	76	76	83	79
V Scottish wrought iron	73	73	71	73	75
W Ingot iron	104	107	104	105	106

It should be noted that the superiority of British wrought irons to mild steel is also shown in cases where the mill scale has been removed from the specimens before exposure. The effect of the initial surface condition of the material will be discussed later in Section 6; for the time being the point is adequately demonstrated by the results obtained at Sheffield given in Table IX. Here the losses in weight of specimens exposed in various surface conditions are expressed as percentages of the corresponding losses of similar mild-steel specimens. For any particular material the ratio is reasonably independent of the surface condition. The sole exception is the Swedish wrought iron *R* exposed in the as-rolled condition; the reason for this discrepancy has already been explained.

It seems, therefore, that whilst the nature of the mill scale on British wrought iron may be a contributory factor to their

superior resistance to atmospheric corrosion as compared with mild steel, it is by no means a complete explanation of the difference.

(ii) *Mechanical Protection by the Slag*.—It has been suggested¹ that the slag particles present in wrought iron, which are generally elongated as lamellæ in the direction of rolling, may obstruct the penetration of corrosion inwards and thereby increase the resistance of the material to attack. In this connection it is well known that, as compared with mild steel, corroded wrought-iron objects such as chain have a grooved appearance corresponding with their fibrous structure.

In some tests on wires an attempt was made to test this hypothesis by adopting a method of piling that would result in the slag (and mill scale) particles being disposed tangentially in concentric circles at short distances apart throughout the cross-section of the wire.² The results of exposure tests³ have failed to show any improvement from this course, as compared with wire of similar composition produced by ordinary methods of piling. Admittedly the experiment is not conclusive, but the result is supported by the fact that the resistance of a given type of wrought iron to atmospheric corrosion is not markedly affected by the number of times that it is worked or by the make-up of the final mill pile; experimental results on the latter subject will be found in Section 8.

Thus, although it is conceivable that the slag particles present in wrought iron may assist corrosion resistance by mere mechanical obstruction, there is no experimental evidence of this in the case of resistance to atmospheric attack.

(iii) *Phosphorus Content of the Wrought Iron*.—The third hypothesis is that British wrought iron owes its increased resistance to corrosion to its higher phosphorus content as compared with ordinary mild steel. There is evidence that an increase in the phosphorus content beyond the normal limits specified for mild steel increases its resistance to atmospheric corrosion; for instance, this fact has been utilised in proprietary steels in Germany and the United States, where it is claimed that the beneficial effect of small additions of copper, alone or with chromium, on the corrosion resistance of mild steel is increased by the simultaneous presence of phosphorus to the amount of some 0.1–0.15%. On analysis, normal British wrought irons show phosphorus contents of the order of 0.2–0.3% (Table II.). Whilst it is obvious that much of this phosphorus is derived from the slag, it is probable that the phosphorus content of the metallic matrix is higher than is usual in ordinary mild steel, and it may well be that the increased corrosion resistance of British wrought iron results from this cause. The fact that the pure Swedish wrought iron is markedly inferior in this respect fits in with this explanation, since its phosphorus content is low, 0.05%,

¹ See K. G. Lewis and U. R. Evans, Second Report, *loc. cit.*, p. 209.

² Third Report, *loc. cit.*, p. 188.

³ Fifth Report, *loc. cit.*, p. 263.

a figure of the same magnitude as that for mild steel. On the other hand, it should be pointed out that, as will be discussed later, Aston-Byers iron, an artificial wrought iron essentially made by the mechanical admixture of a dead mild steel with a synthetic slag, contains a percentage of phosphorus, 0.14%, intermediate in magnitude between those of mild steel and of British wrought irons, yet despite this fact its corrosion resistance is inferior to that of mild steel (Table VII.). It may be that in this case the phosphorus is wholly present in the slag and that during the comparatively brief mixing process there is no appreciable enrichment of the phosphorus content of the ferrite itself.

On the whole it may be said that, whilst all three factors, resistant mill scale, mechanical obstruction by the slag particles and the phosphorus content, may contribute to the increased corrosion resistance of British wrought iron, as compared with mild steel, the effect of the phosphorus content is probably the most important.

(b) *Ingot Iron.*

There is no evidence whatever that the resistance to atmospheric corrosion of ingot iron, which is essentially a dead mild steel in which the carbon, manganese, phosphorus, silicon and sulphur contents have been reduced to the lowest practicable limits, is superior to that of mild steel itself (Tables VI. and IX.). Indeed, if anything, over long periods of exposure the advantage lies with mild steel.

It is true that in certain short-period tests on as-rolled specimens ingot iron lost less in weight than mild steel, but this was due to the greater protective effect of the mill scale on the former, an effect which, as has been shown, may prove disadvantageous under certain conditions (*cf.* the results for Calshot, Table VI.). In a test on sand-blasted specimens over one year at Sheffield,¹ ingot iron lost 217 g. and the standard mild steel X 204 g.; incidentally, in this test the losses in weight of specimens exposed with the mill scale were 214 g. and 218 g., respectively, for the two materials.

(c) *Aston-Byers Iron.*

So far as resistance to atmospheric corrosion is concerned, Aston-Byers iron cannot be regarded as a satisfactory substitute for British wrought irons manufactured by the normal puddling processes. This is surprising, because, as regards analysis, slag content, mechanical properties and microstructure, there is a great degree of similarity between the two types of material.²

¹ Fifth Report, *loc. cit.*, Table XIII., p. 39.

² Fifth Report, *loc. cit.*, p. 193.

It may be recalled that Aston-Byers iron is a synthetic wrought iron made by a special process, which consists of pouring dead mild steel, made by the acid Bessemer process, into a bath of molten synthetic slag. The resulting mass of metal and slag is pressed into a bloom, which can then be worked by rolling and piling in the same way as ordinary wrought iron.

The results of tests over five years at Sheffield (Table VII.) show that Aston-Byers iron proved approximately 10% more corrodible than mild steel itself, whereas in these particular tests Staffordshire wrought iron lost from 25% to 36% less weight than mild steel. Hence, as regards corrosion resistance, Aston-Byers iron is to be classed with ordinary steels rather than with wrought irons. It may be added, without going into detail, that this conclusion is confirmed by the results of similar tests over shorter periods, of other series of loss-in-weight tests on small pieces of $2 \times \frac{1}{8}$ -in. strip and of experiments in which the decrease in breaking load of materials in the form of wire was determined.

5.—EFFECT OF LOW PERCENTAGES OF ALLOYING ELEMENTS ON THE RESISTANCE OF IRON AND STEEL TO ATMOSPHERIC CORROSION.

(a) *General Remarks.*

The conclusions to be drawn in this Section concerning the effect of low percentages of alloying elements on the resistance of iron and steel to atmospheric corrosion are based in the main on two distinct series of experimental results :

(i) Exposure tests at a number of stations for periods up to five years on a number of low-alloy steels, chiefly of the copper and/or chromium type specially prepared under industrial conditions for test by the Committee. Full details of the production, analyses and properties of these steels have been published in the Committee's Reports; a summary of essential data will be found in Table II. For the benefit of those who may not have access to earlier publications, it may be noted that the several series of steels concerned were prepared from the same basis casts and differ only in their content of alloying material. For instance, steels X, Y and Z (Tables II. and X.) are identical except for their different copper contents.

(ii) Exposure tests on a number of commercial low-alloy steels, chiefly of American origin, placed at the disposal of the Committee by the Institute of Welding. The latter were primarily interested in an investigation of their welding properties, but it was felt that it would be in the general interest to obtain data for their comparative resistances to atmospheric corrosion. In view of the limited quantity of material available, these tests are being made at Sheffield only. So far, results after one year's exposure have been

obtained, but the tests will be continued up to a total period of five years with another set of specimens.

The general finding resulting from these experiments may be summarised broadly as follows :

It is possible by the addition of small quantities of suitable alloying elements to ordinary mild steel to produce structural steels of which the resistance to atmospheric corrosion is up to twice as great as that of the unalloyed steel. Since the improvement in corrosion resistance is accompanied by an enhancement of mechanical properties of corresponding magnitude and since these improvements are obtained at a remunerative cost in terms of the alloying elements used, there should be a wide field of usefulness for such steels.

(b) *Effect of Copper.*

The Committee's tests have fully confirmed the pioneer work of the American Society for Testing Materials and individual American investigators which led to the recognition of the beneficial effect of a small percentage of copper in iron or steel on its resistance to atmospheric attack. This is evident from the results given for steels *Y* and *Z* in Tables VI. and X., for steel *ZK* in Table XI. and for Swedish wrought iron *S* in Tables VI. and XI.; other data pointing to the same conclusion will be found in Table XIII.

In round numbers, the loss in weight of a steel containing 0.2% of copper will be from 70% to 80% of that of an equivalent non-copper-bearing steel exposed under similar conditions; in terms of duration of lives of equal sections the superiority of the copper-bearing steel would be at least 25-50%. This margin is not so great as appears to be indicated by the American work, probably because the present results are calculated from loss-in-weight determinations for specimens $\frac{3}{8}$ in. thick, whereas the American figures relate to thin sheets and are based on observed lives to failure by perforation.

The tests show too that 0.2% of copper is sufficient to ensure the desired improvement, since there is no conspicuous difference between the results obtained for steel *Y*, with 0.2% of copper, and steel *Z*, with 0.5% (Table X.).

It should be emphasised that the beneficial effect of copper additions is evident only in the case of steel or iron freely exposed to the atmosphere.

In the Dove Holes Tunnel, for instance, where there is no rainfall and a thick layer of soot and rust builds up on the specimens, the presence of copper in the steel has little or no effect (Table X.). It is possible that the same would hold true for conditions of outdoor exposure in which scale rust formed on the steel, but, as already stated, this has not occurred in these experiments.

The effect of the addition of copper to Swedish wrought iron

TABLE X.—*Effect of Copper Additions on the Atmospheric Corrosion of Mild Steel. (Part I., 5 Years' Exposure.)*

Specimens exposed with mill scale.

Home.			Overseas.				
Station.	Corrosion Rate of Steel X (On 0.02%), Mils per year.	Relative Corrosion (Steel X = 100).		Station.	Corrosion Rate of Steel X (On 0.02%), Mils per year.	Relative Corrosion (Steel X = 100).	
		Steel Y (On 0.2%).	Steel Z (On 0.5%).			Steel Y (On 0.2%).	Steel Z (On 0.5%).
Calshot	1.62	81	78	Abisko	0.27	62	69
Dove Holes Tunnel	2.39	92	96	Apapa	0.77	80	83
Llanwrtyd Wells	1.22	82	85	Aro	0.45	82	89
Motherwell	2.15	78	75	Basrah	0.46	88	84
Redcar	1.92	84	84	Congella	1.82	86	77
Sheffield	4.30	80	79	Khartoum	0.03	144	129
Woolwich	2.26	75	74	Singapore	0.62	77	75

is particularly marked. Whereas after five years' exposure at Sheffield the corrosion of the ordinary Swedish wrought iron *R* was 155% of that of the standard mild steel *X*, that of Swedish wrought iron *S*, prepared from the same basis material but containing 0.6% of copper, was only 68% and considerably less than that of the copper-bearing steels *Y* or *Z* (Table VI.).

The following generalisation seems justified by the data given in Table VI. :

The addition of low percentages of copper to mild steel has the effect of improving the resistance of this material to atmospheric corrosion to a degree which renders this comparable with that of unalloyed British wrought irons. It may be added that the results of atmospheric corrosion tests on wires¹ show that the effect of adding small percentages of copper alone to British wrought iron renders the corrosion resistance of this material comparable with that of mild steel containing *both* copper and chromium.

(c) *Effect of Chromium.*

The effect of the presence of small quantities of chromium in steel is illustrated by the data given for steel *K* in Table XI. This steel differs from the standard unalloyed steel *X2*² in containing 1.0% of chromium; its loss in weight after five years' exposure at Congella or Sheffield was approximately 60% of that of the standard steel.

Hence the addition of even a low percentage of chromium to steel improves its resistance to atmospheric corrosion considerably.

(d) *Joint Effect of Copper and Chromium.*

Reference to Table XI. shows that, whilst the effects of copper and chromium when present simultaneously are supplementary, they are not fully additive. Three distinct copper-chromium steels were tested, *L*, *M* and *N*; each contains 0.5% of copper, but the chromium content is 0.6% for *L* and *M* and 1.0% for *N*. There is a difference too in manganese content, which is 0.6% for *L* but 0.8–0.9% for *M* and *N*. Comparison of the results for these steels amongst themselves and with those for steel *K* (1.0% of chromium but no added copper) and *ZK* (0.5% of copper, but no added chromium) shows that :

(i) The optimum corrosion resistance is obtained, as might be expected, in the most highly alloyed material, steel *N*, with 0.5% of copper, 1.0% of chromium and 0.8% of manganese. (The effect of manganese will be discussed later.)

(ii) Steels *L* and *M*, containing 0.6% of chromium with 0.5% of copper, are roughly equivalent to steel *K*, which contains 1.0% of chromium alone.

¹ Fifth Report, *loc. cit.*, p. 260, and further unpublished data.

² A repeat cast identical with steel *X*, as shown by metallurgical examination and test data (*cf.* footnote to Table XI.).

(iii) The resistance of steel *N* over five years' exposure is approximately double of that of the unalloyed basis steel *X2*. Forward reference to the results given in Table XIII. for the steels obtained from the Institute of Welding indicates that it is probable that an increase in the silicon and phosphorus content of this steel would result in an even greater corrosion resistance. It will be seen from Table XIII. that the copper-chromium-silicon-phosphorus steel *WH* was 10% less corroded than the copper-chromium steel *DN*. The former contains more silicon (0.46%, as compared with 0.05%) but less manganese (0.28%, as against 0.84%); further, the phosphorus content is 0.15%, whereas that of steel *DN* is the normal limit for structural steel, i.e., 0.06% at the most.

(e) *Effect of Silicon.*

The series of steels prepared for test by the Committee were not specifically intended to study the influence of silicon on the resistance of steel to atmospheric corrosion, but, despite this, some interesting indications can be drawn as to its probable effect. For instance, steels *X2* and *XK* (Table XI.) differ only in that the former contains 0.02% of silicon and the latter 0.10% (Table II.); in steelmaking parlance the first steel is "balanced," the second "semi-killed."

The experimental fact is that the steel containing 0.10% of silicon has corroded 11% less than that containing only 0.02% of silicon.

On the other hand, there is no appreciable difference in the behaviours of steels *O* and *ZK* (Table XI.). Comparison of their analyses (Table II.) shows differences in silicon and manganese contents which are, respectively, 0.33% and 1.56% for steel *O*, and 0.12% and 0.60% for steel *ZK*. Steel *O* is "fully-killed" and steel *ZK* "semi-killed"; moreover both contain 0.5% of copper.

It is obvious that, to sort out the effect of each individual element, exposure tests on specially prepared series of steels with appropriate variations in analysis would be needed; as a matter of fact, the Committee have arrangements for such tests in hand. Meanwhile, it may tentatively be concluded that the addition to steel of small amounts of silicon (and possibly of other deoxidising elements) will have a generally beneficial effect in increasing the resistance to atmospheric corrosion.

(f) *Effect of Manganese.*

The only clear-cut comparison relating to the effect of manganese is the relative behaviour of steels *L* and *M*. Both steels contain 0.6% of chromium and 0.5 % of copper, but steel *L* has 0.58% and steel *M* 0.89% of manganese (Table II.). In the atmospheric corrosion tests (Table XI.) there was no significant difference between

them. Further data relating to the effect of manganese will be given later. Provisionally it may be stated that :

In the range of steels tested by the Committee, variations in the manganese content above that required to produce a satisfactory steel have not been found to influence the resistance to atmospheric corrosion to any marked extent.

(g) *Effect of Arsenic.*

It is not unusual for appreciable quantities of arsenic, 0.1% or more, to be present in mild steel. Some indication of the effect of this element on resistance to atmospheric corrosion is given by the results obtained for two steels *P* and *Q*, taken from steelworks' stock, which had high arsenic contents (Table II.). Steel *Q* contains 0.10% of copper, which is probably sufficient to improve its corrosion resistance appreciably without giving it the fully increased corrosion resistance of a true copper-bearing steel. Reference to Table XII. shows that this steel is equal or superior to steel *Y*, containing 0.22% of copper. Since, in addition, steel *P*,

TABLE XII.—*Effect of Arsenic Content on the Atmospheric Corrosion of Mild Steel.*

Specimens exposed with mill scale.

Station.	Duration of Test. Years.	Corrosion Rate of Steel X (As 0.05%, Cu 0.02%). Mils per year.	Relative Corrosion.		
			Steel P (As 0.13%, Cu 0.05%).	Steel Q (As 0.12%, Cu 0.10%).	Steel Y (As 0.05%, Cu 0.22%).
Khartoum .	5	0.03 ¹
Sheffield .	5	4.30	92	81	80
Singapore .	5	0.53	83	70	...
Llanwrtyd Wells .	5	1.26	...	74	84

¹ The corrosion rate is too small to warrant any comparison between the different steels, which were only partially descaled after 5 years' exposure.

with 0.13% of arsenic and 0.05% of copper, is distinctly superior to the standard low-copper steel, it may be concluded that :

The presence of small percentages of arsenic in steel increases its resistance to atmospheric corrosion.

This is in line with the known inhibitive effect of arsenic, present either in the metal or in the solution itself, on the rate of corrosion of steel in acid solutions.

(h) *Effect of Nickel and Other Elements. (Tests on Steels from the Institute of Welding.)*

In conclusion, a brief account will be given of the test results obtained on a number of proprietary low-alloy steels received from

the Institute of Welding. These are of interest inasmuch as they relate to a wider range of compositions than have so far been prepared for the Committee's main field tests and also because they confirm conclusions drawn from previous work.

(i) *Experimental Details.*—During 1940 the Committee received from the Institute of Welding specimens of eleven low-alloy steel plates of British and American origin the welding properties of which were being thoroughly examined by that Institute. It was considered that it would be a useful supplement to this investigation if the Corrosion Committee conducted some atmospheric corrosion tests on the same steels. Accordingly arrangements were made to expose two sets of these specimens in the standard manner at the Sheffield corrosion station. This was done on 12th August, 1940. One set of two specimens of each steel was exposed in the sand-blasted condition and the other set, also of two specimens, was exposed in the as-rolled condition.

Similar sets of specimens of the four types of steel plate built into the coal wagons that are under investigation by the Sub-Committee on Low-Alloy Steels¹ and of the Committee's standard mild steel X2 were also included in this series. All specimens were cut to the standard size, 15 × 10 in., but the steels from the Institute of Welding are $\frac{1}{2}$ in. thick and the four wagon steels $\frac{1}{4}$ in. thick, as compared with $\frac{3}{8}$ in. for the Committee's standard mild steel X2.

It was planned to expose the set of sand-blasted specimens for one year and the set of as-rolled specimens for five years. Consequently, the former set was removed on 12th August, 1941; the latter set is still exposed.

(ii) *Results.*—The results of the tests on the sand-blasted specimens exposed for one year are given in Table XIII. The steels are arranged in order of merit, and, in conformity with other Tables, their losses in weight are expressed as a percentage of that of the standard mild steel X2. It may be noted that the corrosion rate of this steel, 4.51 mils per year, is in good agreement with a previous determination at Sheffield for sand-blasted specimens over a period of one year, which gave a value of 4.87 mils per year.²

Five nickel or nickel-copper steels head the list. Corrosion

¹ No details of the activities of the Sub-Committee on Low-Alloy Steels have been given in previous Reports of the Committee. This Sub-Committee was formed in June, 1938, under the Chairmanship of Mr. T. Henry Turner, to arrange for the conduct of service tests on promising low-alloy steels, as distinct from tests on small specimens. The tests referred to here are concerned with the behaviour of four types of steel plate, of ordinary, copper-bearing, copper-manganese and copper-chromium steel, that have been built into the floors of 100 hopper mineral wagons, with the collaboration of the London and North Eastern Railway Company. These wagons have now been kept under observation for three years and a report on the test will be published in due course.

² The equivalent corrosion rate for steel X2, sand-blasted, in Table XIII. of the Fifth Report (*loc. cit.*, p. 39).

resistance probably increases with nickel content, since the best steel of all, *WE*, contains the highest amount of nickel, 3.12%; this steel is approximately twice as resistant as the unalloyed standard steel *X2*. It is also apparent that the effects of copper and nickel reinforce each other; in fact, if the effect of all other elements is ignored, the results of the first four steels can be approximately deduced on the assumption that 1% of nickel reduces the corrodibility by about 17% and 1% of copper does so by about 10%, *when both alloying elements are present together in amounts of this order of magnitude*. It is noteworthy, too, that the wide differences in the carbon contents of the otherwise similar nickel-copper steels *WN* and *WP* have had no effect on their resistance to corrosion.

Thus, the presence of small percentages of nickel in steel increases its resistance to atmospheric corrosion and reinforces the beneficial effect of copper additions.

The chromium-copper-silicon-phosphorus steel *WH* occupies a high position in the order of merit and has proved superior to the plain copper-chromium steels *WG* and *DN*; as already mentioned, this is probably attributable to the higher silicon and phosphorus contents of steel *WH*.

The results for the pairs of steels *WG* and *DN*, *ZKF* and *WB*, of comparable analysis in each case, agree reasonably well, as indeed they should, since the members of each pair, although obtained through different sources, were originally made by the same manufacturers.

The remaining steels consist of several copper-bearing steels and a series of carbon steels. In conformity with the results already reported, the copper-bearing steels have suffered 20-30% less corrosion than the ordinary steels but have proved less resistant than the copper-chromium steels. For instance, the superior resistance of steel *WK* to steel *YF* is no doubt due to its chromium content, 0.45%; its high silicon content, 0.78%, may also have been a contributory factor, but no evidence is available as to the probable effect of its zirconium content, 0.10%.

Finally, it will be noted that wide variations in the manganese content have had no appreciable effect on the corrosion resistance of otherwise approximately equivalent steels. For instance, the difference between the Admiralty *D* steel *WC* (manganese 1.40%), the carbon-manganese steel *WA* (manganese 1.54%) and the standard mild steel *X2* (manganese 0.57%) is at most 5%; in the case of steel *WC* this could be accounted for by the appreciable quantity of arsenic present (0.11%). Or again, there is only a 3% difference in the relative corrodibilities of the copper-bearing steels *WB* and *YF*, with 1.41% and 0.56% of manganese, respectively; the 0.09% of silicon present in the former would largely account for this.

TABLE XIII.—*Comparison of Various Commercial Low-Alloy Steels from the Institute of Welding, &c.*

All specimens shot-blasted before exposure. Duration and place of test, one year at Sheffield.

	Steel. Reference and Type.	Analysis.						Other Elements, ¹ %.	Relative Corrosibility (Steel X ₂ = 100). ²
		C. %.	Mn. %.	Si. %.	Cr. %.	Cu. %.	Ni. %.		
WE	3% nickel	0.31	0.59	0.22	0.10	0.09	3.12	...	49
WN	Nickel-copper (low-carbon)	0.09	0.38	0.14	0.03	0.95	1.96	...	56
WP	Nickel-copper (high-carbon)	0.20	0.70	0.17	0.04	1.05	1.93	...	56
WD	2% nickel	0.20	0.68	0.11	0.01	0.05	2.44	...	59
WL	Cu-Ni-Mo	0.07	0.60	0.03	0.04	1.13	1.31	Mo 0.10	60
WH	Cr-Cu-Si-P	0.08	0.28	0.46	0.82	0.40	0.04	P 0.15	61
WG	Cr-Mn-Cu	0.18	0.82	0.07	0.83	0.31	0.03	...	65
DN	Copper-chromium ³	0.25	0.84	0.05	0.90	0.33	0.03	...	66
WK	Cu-Cr-Si-Zr	0.11	0.55	0.78	0.45	0.16	0.09	Zr 0.10	66
ZKF	Copper-manganese ³	0.19	1.34	0.21	0.08	0.44	<0.01	P 0.05, S 0.05	70
WB	Copper-manganese	0.21	1.41	0.09	0.07	0.52	0.07	P 0.06, As 0.05	74
YF	0.35% copper ³	0.17	0.56	0.03	0.04	0.35	0.01	...	76
DX	Mild ³	0.19	0.46	0.02	<0.02	0.07	0.04	...	92
WC	Admiralty D	0.24	1.40	0.06	0.03	0.04	0.07	As 0.11	95
WA	Carbon-manganese	0.19	1.54	0.09	0.08	0.03	0.04	S 0.05, As 0.05	97
X ₂	Corrosion Committee's standard mild steel	0.24	0.57	0.02	0.04	0.02	100

¹ Present in amounts of 0.05% or more.² The loss in weight of steel X₂ was equivalent to an annual corrosion rate of 4.51 mils.³ Included in the coal-wagon tests of the Sub-Committee on Low-Alloy Steels.

6.—EFFECT OF THE INITIAL SURFACE CONDITION ON THE ATMOSPHERIC CORROSION OF IRON AND STEEL.

(a) *General Remarks.*

As mentioned in the Introduction, the surface condition of the specimens prior to exposure was varied in many cases (Table III.), since it was thought possible that this might have some effect on the results obtained. For instance, it is known that the maximum corrosion resistance of certain rust-resisting chromium steels is attained only when the material is in the fully polished condition. This result is connected with the production by polishing of an intact and resistant oxide film on the surface of the metal, and it was not inconceivable that a similar, though possibly less marked, effect might be evidenced in the case of ordinary irons and steels. Consequently, similar sets of specimens of the same test materials were exposed not only in the normal as-rolled condition but also after they had been polished, machined or descaled by sand-blasting or pickling.

The results obtained from this section of the work will be briefly reported here, but it may be stated at once that :

(i) Although the surface condition of the specimen may play a part in retarding the initiation of atmospheric corrosion—for instance, mill scale or the adherent sand deposit left after sand-blasting may do so—such effects are generally transient and become relatively unimportant over long periods of exposure in corrosive atmospheres.¹

(ii) There is no evidence—again with reference to long periods of exposure and corrosive atmospheres—that the order of resistance of different materials to atmospheric corrosion is appreciably affected by differences in their surface condition before exposure, provided that this surface condition is the same for all.

(b) *Comparison of Surfaces with and without Mill Scale.*

When examining the experimental data as to the relative behaviour of specimens exposed with or without the mill scale there are at least three variables to consider : (i) The corrosion station, (ii) the material, and (iii) the surface condition ; in a few cases there is a fourth, the duration of exposure, although most of the data refer to a standard period of five years. In all, 202 combinations of the above are covered by the experimental results to date, *i.e.*, 202 direct comparisons have been made of similar materials exposed with and without the rolling scale. Presentation of the data in full would involve several cumbersome Tables and would not be justified under present circumstances, particularly

¹ In this connection, by "corrosive atmospheres" is to be understood one in which the rate of corrosion of ordinary mild steel is at least 1 mil per year, which rate of corrosion is intermediate between those observed at Singapore and at Llanwrtyd Wells (Table IV.).

as the results are largely negative. They may briefly be summarised as follows :

In 158 out of 202 cases, *i.e.*, 78% of the total, the difference between the losses in weight of specimens of the same material in the as-rolled and descaled conditions, respectively, is either less than the weight of the mill scale initially present on the former ¹ or does not exceed 10% of the actual loss suffered by the specimens exposed with the mill scale. In these cases it may be said that the presence of the mill scale has had no appreciable effect on the results.

Of the other 44 cases, a number may fairly be attributed to experimental error. Part of the remainder are explicable on the grounds that the losses in weight of the specimens exposed with mill scale were abnormally high, owing to the formation of scaly rust, for instance, on the wrought irons and ingot iron at Calshot. There were 13 cases in which the corrosion of descaled specimens of steels X, Y or Z (7 of X, 2 of Y and 4 of Z) was excessively low as compared with that of the normally rolled specimens; 7 of these occurred at Calshot. It is tempting to assume that in these cases, too, the corrosion of the as-rolled specimens had been stimulated by the accumulation of scaly rust on them, as on the wrought irons and ingot iron. There was, however, no visible evidence of this, and the losses in weight during the derusting process fail to show that there were heavier quantities of rust on the as-rolled than on the descaled specimens.²

In cases where the rate of corrosion falls below a minimum value, say approximately 1 mil per year, and in particular where the mill scale is not shed completely before the end of the exposure period, there may be marked relative differences between the losses in weight of specimens exposed with the mill scale and without it. Under such conditions the relative corrodibilities of dissimilar materials, as determined by their relative losses in weight, will vary according to the surface condition in which they are tested. This is true to some extent for all the overseas stations with the exception of Congella and possibly of Singapore, but, even in these cases, although the quantitative ratios may vary, the order of merit generally remains the same, *e.g.*, copper-bearing steel will prove superior to ordinary steel. Obviously when the rate of corrosion is small, differences in the corrodibility ratios are of little practical significance. It may, therefore, be concluded that as a general rule the corrosion rate over long periods is not markedly affected by

¹ With few exceptions, the losses in weight of the descaled specimens were less than that of the corresponding normal as-rolled surface. The weight of mill scale per specimen varied from 40 g. to 60 g. according to the material, and, since this is shed when the iron corrodes, differences up to this amount have no significance.

² As deduced from the differences in the weights of the specimens as received after exposure and after the final cleaning, respectively. See Appendix A, and for details of the Calshot results Fifth Report, *loc. cit.*, Table XI., p. 32.

TABLE XIV.—Comparison of Pickled, Sand-Blasted, Machined and Polished Surfaces.

Material.	Station.	Loss in Weight of Normal As-Rolled Specimens, G.	Relative Corrodibility. ¹			
			Pickled.	Sand-Blasted.	Machined.	Polished.
R	Sheffield	1380	87	84	86	78
S	Sheffield	608	101	98	95	95
T	Sheffield	685	99	98	106	100
V	Sheffield	645	100	96	99	102
W	Sheffield	922	103	99	100	101
X	Calshot	335	64	62	73	68
	Llanwrtyd Wells	252	75	69	81	77
	Sheffield	889	100	98	99	98
	Woolwich	468	87	84	79	76
	Calshot	272	71	71	83	75
Y	Llanwrtyd Wells	208	85	79	89	89
	Sheffield	713	101	98	105	104
	Woolwich	349	84	81	88	82
	Calshot	289	68	67	79	72
	Llanwrtyd Wells	213	81	79	91	87
Z	Sheffield	698	101	99	106	105
	Woolwich	345	82	79	87	79

¹ The loss in weight of the normally rolled specimens is taken as 100.

the surface condition before exposure, if due allowance is made for the weight of mill scale on as-rolled surfaces, and that the relative corrodibilities of different materials are not appreciably affected thereby in long-period tests in corrosive atmospheres.

(c) *Comparison of Pickled, Sand-Blasted, Machined and Polished Surfaces.*

Four different types of descaled surfaces were used in the tests (Table III.). With the first two, pickled and sand-blasted, the aim is to remove the mill scale, by chemical or mechanical means, respectively, with the minimum accompanying loss of metal proper; in the preparation of the last two, machined or polished surfaces, surface layers of appreciable thickness are removed from the metal itself. In machining, the removal of metal is accompanied by the production of a comparatively rough and torn surface.

The effect of these various surface conditions is illustrated by the results given in Table XIV., for series of tests in which all four were exposed side by side. In other series of tests, two or more of the surface conditions were exposed simultaneously, but since the results tally with the conclusions drawn from Table XIV., it is unnecessary to give details of them. The main conclusions to be drawn from this Table are :

(i) The effect of differences in the surface condition of descaled specimens is not pronounced and is almost negligible on wrought irons and ingot irons exposed at Sheffield, where the corrosive attack was severe.

(ii) In the case of steels X, Y and Z, which, although differing in copper content, were all prepared from the same basis cast and rolled from the same type of semi-rimming ingot, sand-blasted specimens suffered less and machined specimens more corrosion than the pickled or polished specimens. The average relative corrodibilities for the twelve series concerned are : Sand-blasted 80.5; pickled 83.3; polished 84.3; machined 90.5.

The inferior corrosion resistance of the machined surface may be due to (a) its greater roughness and (b) the fact that the machining operation removed the thin rim of purer material on the immediate surface of the specimens. The fact that there was no appreciable difference between the various surfaces in the case of the four wrought irons points to the conclusion that the latter factor is more important than the roughness of the surface.¹

The higher resistance of the sand-blasted specimens may be attributed to the thin layer of sand left on them after treatment, which retards corrosion in the early stages.

¹ Ingot iron is rolled from a rimming ingot, but the thickness of the rim is much greater than in the case of the steels X, Y and Z. On the actual specimens it was approximately $\frac{1}{16}$ in., i.e., the same thickness as the nominal depth of the machining cut, so that it is uncertain whether the rim was penetrated or not by this operation.

7.—TIME NECESSARY TO REMOVE MILL SCALE FROM STEEL BY WEATHERING IN THE ATMOSPHERE.

In the course of the routine inspections at the various corrosion stations, the amount of mill scale, if any, remaining on specimens exposed in the as-rolled condition was noted. Detailed records of the progress of descaling with time will be found in the Committee's earlier Reports, but it may be useful to give here a rough summary of the duration of exposure required to remove the mill scale from ordinary mild steel by the natural weathering process in different climates. This is done in Table XV., where the figures refer to the

TABLE XV.—*Duration of Exposure Necessary to Remove 95% of the Mill Scale from Mild Steel (Average Value for Steels X, Y and Z).*

Home.			Overseas.		
Station.	Corrosion Rate. Mils per year.	Time for 95% Descaling. Years.	Station.	Corrosion Rate. Mils per year.	Time for 95% Descaling. Years.
Calshot	1.62	1.1	Abisko	0.27	> 5.0
Dove Holes Tunnel	2.39	... ¹	Apapa	0.77	> 3.5
Llanwrtyd Wells	1.22	1.0	Aro	0.45	> 5.0
Motherwell	2.15	1.3	Basrah	0.46	> 5.0
Redcar	1.92	0.6	Congella	1.82	0.9
Sheffield	4.30	1.0	Khartoum	0.03	> 5.0
Woolwich	2.26	0.4	Singapore	0.62	3.0

¹ No estimate could be made, since the specimens became covered with soot and rust.

observed durations of exposure necessary to remove 95% of the mill scale from mild steel; the values given are means for the three steels X, Y and Z.

The rate of descaling naturally varies with the corrosiveness of the atmosphere, as is evident from the experimental results. At four overseas stations, Abisko, Aro, Basrah and Khartoum, five years' exposure was insufficient to produce complete descaling; three years were needed at Singapore, whilst the average figure for the six home stations and Congella was 0.9 year. It will be understood that, particularly at the home stations, the season of exposure plays an important part, since conditions are much more corrosive in winter than in summer, but in round figures it may be said that to remove the mill scale entirely from ordinary mild-steel flats, as tested by the Committee, about one year's exposure in home atmospheres would be required. In practice, the time might be rather less, since the specimens on which these estimates are based could not be taken down for the wire-brushing which usually accompanies commercial descaling by weathering; this treatment might have removed some of the residual mill scale.

The character of the mill scale, which will be influenced by the type and size of section and the rolling conditions, will affect the

results, but it is thought that the figures given may be regarded as reasonably representative. It should be added that, regarding the results as a whole, no marked difference was observed in the rates of descaling of ordinary and of copper-bearing steels. There was certainly no evidence that the presence of copper in steel retards the rate at which it sheds its mill scale. If anything, the copper-bearing steels were descaled more rapidly than the ordinary steel, which would agree with the fact that the mill scale was thinner on the former.¹

8.—EFFECT OF SUNDRY VARIABLES (METHOD OF PILING WROUGHT IRON; DIFFERENT CONDITIONS OF EXPOSURE).

(a) *Effect of the Method of Piling Wrought Iron.*

The methods adopted for the manufacture of the British and Swedish wrought irons exposed in these experiments, which were typical for materials of their respective classes, have been described in earlier Reports.² In principle they are all similar. A spongy mass of almost carbon-free iron is produced from the original charge of pig iron by treatment with suitable oxidising agents in a small furnace. In the case of British irons, this mass is broken up into "balls" of convenient size, which are roughly squared, singly or after pairing, under a steam hammer and then rolled into "puddled bars." The puddled bars are sheared into pieces of convenient length, which are then arranged on top of each other so as to form a laminated block or "pile." The piles are heated to a white-heat and rolled down, usually after an initial hammering, to bars, which in Staffordshire are known as "ball-furnace bars" and in Scotland as "double-forged bars." The process of piling and of rerolling may then be repeated, using these ball-furnace bars either alone or in admixture with puddled bars. Since, further, when building any pile the pieces of bar used may be arranged with their longitudinal axis either along ("straight" piles) or across ("crossed" piles) the length of the pile, a number of variants of the piling process are possible. In practice, the procedure followed is determined by the section and the required quality of the iron.

The object of these treatments is to remove the superfluous slag present in the original ball and produce a uniform and compact wrought iron with a good surface and good mechanical properties. Since the slag content of Swedish wrought iron is much lower than that of British wrought iron, it is unnecessary to work it to the same extent and the amount of repiling needed is much less. In fact, in the case of $10 \times \frac{3}{8}$ -in. flats, as used in the Committee's tests, no repiling is usual, so that, on removal from the furnace, the resulting iron was hammered (in one lot, not as a number of

¹ At least, as judged by the average losses in weight on sand-blasting numerous specimens of each type.

² Second Report, *loc. cit.*, p. 19.

TABLE XVI.—*Effect of Method of Manufacture (Piling, &c.) on the Resistance of Wrought Iron to Atmospheric Corrosion.*

Specimens exposed with mill scale. Duration of tests, 5 years.

Bar Refer- ence.	Specimens ¹ Cut from—	Loss in Weight. G.									
		Sheffield. Part IV.	Llanwryd Wells. Parts I. and II.				Sheffield. Parts I. and II.				
		Aston- Byers Iron H. ²	Swedish Wt. Iron R.	Swedish Wt. Iron S (Cu 0.6%).	Stafford- shire Wt. Iron T.	Scottish Wt. Iron V.	Swedish Wt. Iron R.	Swedish Wt. Iron S (Cu 0.6%).	Stafford- shire Wt. Iron T.	Scottish Wt. Iron V.	
A	Puddled bar . . . Higher rolling temperature	890 ³	289	232	253	267	1380	608	809	774	
B	Straight pile <i>ex</i> puddled bar A . . Reduced rolling temperature	834	283	222	210	199	1217	575	675	606	
C	Crossed pile <i>ex</i> puddled bar A . .	879	213	203	
D	Mixed pile A and B . . .	827	212	216	645	
E	Reduced rolling temperature . . Straight pile <i>ex</i> B . . .	824	204	201	685	644	
F	Reduced rolling temperature . . Crossed pile <i>ex</i> B	192	640	...	

¹ Normal rolling procedure unless otherwise stated.

² Specimens rolled in Great Britain from billets made in the U.S.A. (see Fifth Report, *loc. cit.*, p. 191).

³ Similar specimens rolled in the U.S.A. lost 841 g.

balls) into a bloom. This bloom was cut up into billets, which, after reheating, were rolled directly into the experimental bars.

Reference has already been made (Section 4 (a) (ii)) to the possibility that the corrosion resistance of wrought iron is enhanced by mechanical obstruction resulting from the presence in it of slag particles. If so, it might be influenced by the method of piling used to produce the iron, since this would affect the shape and distribution of these particles. Consequently, it was thought advisable to conduct tests on wrought irons produced by different methods of piling, the general principle adopted being to prepare the majority of specimens of any given iron in the manner regarded as most typical of that particular iron, but to add a number of other specimens prepared by the alternative procedures followed

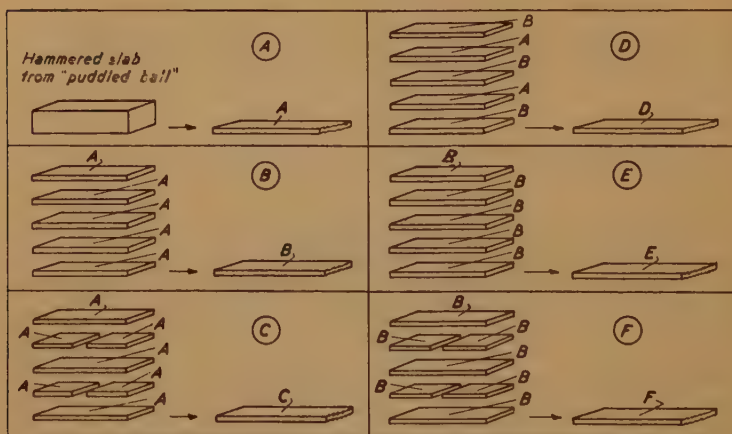


FIG. 4.—Details of Piling the Different Wrought Irons (diagrammatic).
(In C and F the small pieces are at right angles to the long ones.)

for the preparation of the bulk of the specimens of the other wrought irons.

Comparable tests of the different piling procedures have been made at Sheffield and Llanwrtyd Wells over a period of five years. The results are given in Table XVI.; the several methods of piling used are shown diagrammatically in Fig. 4, from which minor details applicable to individual wrought irons only (*e.g.*, differences in the number of individual pieces per pile) have been omitted.

It may be concluded from the results that reworking the iron once improves the resistance to atmospheric corrosion, since the losses in weight of bars marked B are distinctly less than those of the corresponding puddled bars A. Since the difference is much more marked for the British wrought irons T and V than for the Swedish

wrought irons *R* and *S*,¹ it is probable that the main cause of the improvement is the consolidation and smoothing of the surface due to rerolling; as is known, the British puddled bars have a rough and porous surface. There is no evidence that reworking more than once has any additional effect on the corrosion resistance.

(b) *Effect of the Conditions of Exposure.*

It should be remembered, when considering practical applications of the experimental results, that the rates of corrosion observed apply to specimens suspended vertically at a uniform mean height from the ground and freely exposed to the atmosphere, with the minimum of interference from adjacent specimens or stands. Strictly comparable results have thus been obtained for the resistance to

TABLE XVII.—*Effect of Height above the Ground on Atmospheric Corrosion.*

Station.	Number of Cases ¹ in which the more Corroded Specimen of Each Pair is in the—	
	Lower Row (2 ft. 6 in.).	Upper Row (4 ft. 6 in.).
Calshot	25	5
Llanwrtyd Wells	10	10
Sheffield	6	44
Woolwich	0	21

¹ In one case at Llanwrtyd Wells, both specimens lost the same weight and one member of a single pair of specimens has been lost from the Sheffield station.

atmospheric corrosion of the different materials tested, but it is evident that the observed values of the corrosion rate would have been different and that the relative corrodibility of the materials might have been affected, too, if the specimens had been exposed, say, horizontally instead of vertically or at a greater or lesser height. In this sub-section some positional and other factors that may affect the results will be considered.

(i) *Height from the Ground.*—It is known that in the immediate neighbourhood of the ground the velocity of the wind increases with the height above it. Consequently, the rate of atmospheric corrosion might also be expected to vary with the height above ground and, in fact, evidence of this has been found in the present experiments. It will be remembered that the specimens are exposed on the stands in two rows which are approximately 2 ft. 6 in. and 4 ft. 6 in. from the ground, measured to the lower edges. Since

¹ The loss in weight for bar *A* of material *R* at Sheffield was abnormally high, for reasons already given.

duplicates are invariably placed in different rows, it is possible, by comparing their losses in weight, to assess whether there is any difference between the corrosivity of the atmosphere at the two heights. Such a comparison is made in Table XVII. for the larger series of tests undertaken at the four main corrosion stations.

The results are surprising. There is no evidence of any height effect in the rural atmosphere of Llanwrtyd Wells, but there can be no doubt of its existence at the other three stations. At Sheffield and Woolwich, both industrial atmospheres, the variation is in the direction that might be expected on the supposition that corrosion will increase with the volume of air flowing over the specimens, *i.e.*, with the wind velocity or the height from the ground. Contrariwise, it might be argued that increased wind velocity would have the opposite effect by leading to a more rapid drying of the specimens after dew or rain. This might be advanced as an explanation of the diametrically opposite observation at Calshot, where the lower specimens were the more corroded; owing to their position on the spit, the specimens receive quantities of presumably deliquescent salt spray.

It would be unprofitable to carry these speculations further without additional evidence; the main point to note is that these positional effects exist. It should be added that their magnitude, 5–10% at most, is not such as to impair the conclusions drawn from the Committee's work, which are based on mean results for specimens at both heights.

(ii) *Effect of Orientation. Horizontal versus Vertical Surfaces.*—The rate of corrosion of a given material will vary with the angle at which it is exposed, for several reasons. For instance, the slope of the surface will affect the rate at which it dries after rain or dew deposition, both directly as a result of the effect on the drainage, and indirectly because of its effect on the absorption of solar heat. It is probable, too, that scaley rust, which has a damaging effect, will develop more readily on a horizontal than on a vertical surface. On this hypothesis, horizontal surfaces should corrode more than vertical ones. Although this matter has not yet been put to direct experimental test in the present researches, it may be significant that the highest corrosion rates observed for the standard mild steel *X* have applied to specimens exposed horizontally, values of up to 0.0080 in. per year having been recorded as compared with a maximum of 0.0055 in. per year for vertical specimens at Sheffield.¹

G. Chaudron² gives some interesting data on this subject, which are summarised in Table XVIII. These refer to specimens of seven different commercial irons and steels exposed (a) horizontally, (b) at an angle of 45° and (c) vertically. It is clear that the corrosion

¹ Fifth Report, *loc. cit.*, p. 44 and Table XIX.

² "Journées de la Lutte contre la Corrosion," *Chimie et Industrie*, 1939, vol. 41, No. 4 bis, p. 42C.

of horizontal specimens is greater than that of vertical ones; specimens inclined at 45° occupy an intermediate position. Despite the differences in corrosion rates, it does not appear that under these conditions—the specimens were exposed in an industrial atmosphere at Lille—the orientation of the specimens has had any marked effect on the relative behaviour of the different materials. Chaudron also shows that there is an appreciable difference between the losses in weight of the upper and lower surfaces of horizontal or inclined specimens, the lower surfaces being the more corroded, owing to the greater time required to dry after having been wetted.

TABLE XVIII.—*Effect of Orientation on Atmospheric Corrosion (G. Chaudron).*

Ref.	Material Type.	Loss in Weight. G. per sq. dm. per year. ¹		
		Horizontal Specimens.	Inclined Specimens (45°).	Vertical Specimens.
<i>S</i>	"Pure iron"	8.14	6.76	6.28
<i>A</i>	Mild steel	8.10	6.37	6.49
<i>C</i>	(?) Copper-bearing steel	6.65	5.27	5.00
<i>B</i>	Copper-bearing steel	6.47	4.81	4.88
<i>D</i>		6.15	4.81	4.69
<i>E</i>	(?) Copper-chromium steel	5.20	4.54	4.50
<i>H</i>	Copper-chromium steel	5.79	5.00	4.62
	Mean	6.64	5.37	5.21

¹ The specimens were exposed for 12 months; 1 g. per sq. dm. equals approximately 0.5 mil of steel.

These experiments by Chaudron were preliminary to a large series of field tests commenced by the Office Technique pour l'Utilisation de l'Acier in the spring of 1939. Arrangements were made to expose specimens of numerous commercial structural steels in all three orientations mentioned. The work is on such a scale that if, as is hoped, the results become available at the end of the war, they will go far to settle the point under discussion. Meanwhile, it may be assumed that the relative order of merit of different types of material as regards resistance to atmospheric corrosion will not be materially affected by the angle at which they are exposed.

(iii) *Effect of Rust.*—The following two series of observations illustrate the effect of rust on the progress of further corrosion: (1) In September, 1937, two similar specimens of the standard mild steel X (actually old derusted specimens) were fixed in a horizontal position to the base of a wooden stand used for small-scale outdoor exposure tests at Birmingham. Some pieces of scaly rust were placed on one but not on the other; as a result the first specimen dries much more slowly after rain and remains wet for several hours longer.

At approximately yearly intervals the specimens have been removed, lightly wire-brushed and reweighed. Their positions are reversed after each period, and on re-exposure scaly rust is again placed on the same specimen as originally. The losses in weight of each steel over each of the first five exposure periods are given in Table XIX.

TABLE XIX.—*Effect of Scaly Rust on the Corrosion of Mild Steel.*

Exposure Period Ending in—	Loss in Weight. G.	
	No Scaly Rust.	With Scaly Rust.
1938	98	128
39	124	164
40	325	374
41	121	158
42	130	122
Total	798	946

Over the whole five-year period, the specimen with the scaly rust on it has lost 946 g. as compared with 798 g. for the other specimen, *i.e.*, 18% more. The difference is definite in all exposure periods except the last, in which it is in the wrong direction. It is thought that this discrepancy is due to the sheltering of the specimen with scaly rust by an obstruction placed there during the period; to test this, the obstruction will be kept in position during the next exposure period, in which the specimens will be reversed.

(2) Another eight specimens, two each of Aston-Byers iron *H*, Swedish wrought iron *R*, Staffordshire wrought iron *T* and ingot iron *W*—all in the as-rolled condition—were attached in a horizontal position to the base of the same stand in January, 1937. There is about 2 in. clearance between the ground and the lower surface of the specimens and the duplicates of each material are placed symmetrically with respect to the stand to avoid any positional effect.

It has been observed that the rates at which the specimens dry after rain varies for different materials and, further, that the order of drying seems to be characteristic of the material. For instance, the curves in Fig. 5 refer to observations made in February, 1939, and establish the order of drying as : *T* Staffordshire wrought iron (most rapid); *H* Aston-Byers iron; *R* Swedish wrought iron; and *W* ingot iron (slowest). After nearly four years' exposure, in December, 1941, the specimens were removed, wire-brushed and reweighed. The mean losses in weight proved to be : *T* 355 g.; *H* 602 g.; *R* 692 g.; and *W* 844 g. The order of loss in weight agrees exactly with the order of drying.

It is not yet clear whether this is a genuine result or a coincidence, because observations of the drying rates in March, 1942, were erratic

and did not confirm the earlier results. This may be because there had been insufficient time for thick layers of rust to build up on these specimens after the cleaning in December, 1941. Further records will be made in due course, but the results already reported will suffice to draw attention to the possible effects of differences in the types of rust produced on different materials on their rates of drying and thus on their rates of atmospheric corrosion.¹

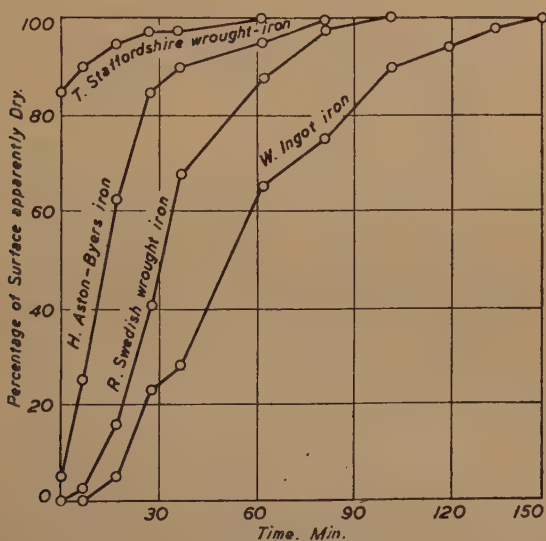


FIG. 5.—Rates of Drying of Different Materials Exposed Horizontally.

9.—PROTECTION OF STEEL BY GALVANISED COATINGS.

Extensive tests on protective coatings of zinc and other non-ferrous metals for mild steel were commenced by the Protective Coatings Sub-Committee in 1939; the results will form the subject of later publications. The present discussion will be confined to results obtained as a direct part of the main atmospheric corrosion tests and will refer to protection by zinc coatings of the hot-galvanised type.

(a) Tests on Galvanised Specimens at Llanwrtyd Wells.

Two sets of hot-galvanised specimens, *i.e.*, twelve specimens in all, were included in the first series of tests on ordinary and copper-bearing steels X, Y and Z, exposed at Llanwrtyd Wells in

¹ Recent observations (January, 1943) show that, whilst the drying curves cross each other at the start, the final order of drying is now the same as in February, 1939, *viz.*: T, H, R, W.

August, 1931.¹ In each set, two specimens of each steel were coated, the difference being that in the second set 0.5% of copper was deliberately added to the zinc bath. The average weight of coating was approximately 2.1 oz. of zinc per sq. ft. of surface, corresponding to a calculated thickness of 0.0035 in.

The specimens have now been under observation for eleven years. The only sign of failure so far noticed is the development of isolated rust spots on the coating, not greater in size than a pin-head. These were first recorded towards the end of the fourth year of exposure. These rust spots have shown no tendency to spread or increase in numbers during the last five years, and it is doubtful whether any practical significance should be attached to them, particularly as the total number on the twenty-four surfaces exposed was only twenty at the last inspection.

In July, 1938, after seven years' exposure, a more direct assessment of the deterioration of the zinc coatings was made. A balance was taken up to the site and the specimens were removed from the stands and weighed; they were wiped over with a duster before weighing, but no attempt was made to remove corrosion products. The losses in weight recorded were equivalent to from 0.072 oz. to 0.160 oz. per sq. ft. of surface, the average value being 0.111 oz. per sq. ft. Any difference between the two types of coating or any effect of the copper content of the steel base was within the experimental error. Although the loss observed would have been greater if the specimens had been fully cleaned before weighing, it is improbable that the magnitude of the rate of corrosion of the zinc coating would have been materially altered, since experience has shown that the bulk of the corrosion product formed by zinc during atmospheric corrosion is removed by the rain water.

It may be anticipated, therefore, that considerable time will elapse before the galvanised specimens at Llanwrtyd Wells fail. More immediate information concerning the behaviour of zinc coatings will be obtained from the tests of the Protective Coatings Sub-Committee already mentioned and can also be deduced indirectly from the results of the routine tests on small zinc specimens, exposed to measure the atmospheric pollution at the corrosion stations, which will now be considered.

(b) *Rates of Corrosion of Solid Zinc.*

It has been the practice throughout these experiments to expose sets of small "pollution" specimens, each 4×2 in., of both ingot iron and zinc, at all testing stations for consecutive periods of one year. This was done primarily to determine the relative corrosiveness of the different atmospheres and to reveal any gross fluctuations in the atmospheric conditions at any given station. It has had the incidental advantage of providing a considerable body

¹ First Report, *loc. cit.*, p. 103.

TABLE XX.—*Rates of Atmospheric Corrosion of Zinc. Probable Lives of Galvanised Coatings.*

Home.				Overseas.			
Station.	Corrosion Rate of Zinc, Oz. per sq. ft. per year.	Ratio of Rates for Ingot Iron and Zinc.	Calculated Life of Galvanised Coating (0.75 oz. per sq. ft.). Years.	Station.	Corrosion Rate of Zinc, Oz. per sq. ft. per year.	Ratio of Rates for Ingot Iron and Zinc.	Calculated Life of Galvanised Coating (0.75 oz. per sq. ft.). Years.
Calshot	0.080	20.1	9	Abisko	0.013	9.8	58
Dove Holes Tunnel	1.92	1.0	0.4	Apapa	0.025	23.9	30
Llanwrtyd Wells	0.073	19.0	10	Aro	0.037	8.5	20
Motherwell	0.103	21.0	7	Basrah	0.026	14.3	29
Redcar ¹	Congella	0.095	20.4	8
Sheffield	0.405	7.5	2	Khartoum	0.012	3.6	63
Woolwich	0.089	26.4	8	Singapore	0.021	16.8	36
Derby	0.183	17.8	4	Berlin-Dahlem	0.065	19.3	12
Frodingham	0.244	20.7	3	Sandy Hook, N.J.	0.062	30.6	12
Sheffield University	0.136	19.4	6	State College, Pa.	0.021	30.9	36
				Pittsburgh, Pa.	0.181	15.1	4

¹ Specimens lost.

of information concerning the rate of atmospheric corrosion of solid zinc and, therefore, indirectly of zinc coatings, which can, as a first approximation, be taken as equivalent to this. Detailed results of these tests on small pollution specimens will be found in Appendix B. Data for the rates of corrosion of zinc, abstracted from these, are given in Table XX.

The rate of corrosion of zinc at all the overseas stations, except Congella, is much lower than the values observed in Great Britain. For instance, at Singapore the annual loss was 0.025 oz. per sq. ft., or at Aro, in Nigeria, 0.039 oz. per sq. ft. Translated into terms of lives of coatings, these figures mean that ordinary commercial galvanised sheets carrying 0.75 oz. of zinc per sq. ft. of surface might be expected to last for 30 or 19 years before serious rusting occurred under these conditions of exposure; indeed, since the rate of corrosion tends to be less over a long period than over a short one, the observed lives might even prove longer than these. Corrosion at the home stations is more rapid, the observed maximum in the open atmosphere being 0.40 oz. per sq. ft. per year at Sheffield; here the life of the commercial coating in question would be rather less than two years, which agrees roughly with practical observations. In the least corrosive home atmosphere, Llanwrtyd Wells, the rate of attack is 0.080 oz. per sq. ft. per year, so that the 0.75 oz. per sq. ft. coating would last about nine years.

Figures for a Berlin suburb and for several test stations of the American Society for Testing Materials are also included. On the whole, they are lower than would be expected for similar types of atmosphere in Britain.

It will be noticed that the rate of corrosion of zinc in the Dove Holes Tunnel was enormous, 1.9 oz. per sq. ft. per year. This is due to the constantly high humidity and sulphur pollution. The zinc corrosion product, essentially a basic sulphate, is deliquescent and absorbs moisture from the atmosphere, with the result that beads of a solution of corrosion product drip continuously from the bottom edges of the specimens. Zinc is obviously useless as a protective under such conditions; in fact, as will be seen from Table XX., it is as corrodible as mild steel itself.

(c) *Comparative Corrosion Resistance of Galvanised and Black Sheets.*

In conclusion it may be profitable to consider one or two practical applications of the results, which are of especial importance now that it is necessary to economise as much as possible both in steel itself and in zinc used for coatings.

Economic Value of Zinc Coatings.—Considering first the case in which sheets are exposed to the atmosphere without a protective paint, it is clear that the effect of using a galvanised sheet is to provide the steel with a thin surface layer of the more resistant metal zinc: further, that if under the conditions of exposure mild

steel corrodes at n times the rate of zinc, then the increase in life to perforation resulting from galvanising could also be achieved by increasing the thickness of the basis mild-steel sheet by n times the thickness of the galvanised coating. The question as to whether the galvanised sheet or the thicker black sheet is the more economical will be determined by the value of n .

Without going into detail, it may be said that, on the basis of market prices prevailing at the outbreak of war, a galvanised sheet would be more economical than an equivalent thicker black one, provided that n was not less than 5, *i.e.*, provided that under the circumstances of use zinc was at least 5 times as resistant to corrosion as mild steel. Reference to Table XX. shows that this condition holds good for all open-air testing stations.¹ The average iron/zinc ratio for all of them is approximately 15. On the other hand, as has been seen, the use of galvanised coatings would not be justified in enclosed polluted atmospheres such as the Dove Holes Tunnel and under certain other industrial conditions.

Probably the greatest value of galvanised coatings is evidenced in the second and much more common case, that in which the sheets are given a protective coat of paint. This is not the place to go into great detail concerning painting, which will be discussed in a second communication dealing with the test results for painted specimens, but it may be remarked that the main difficulty in painting steel successfully is to ensure that the first coat of paint is applied to a good rust-free surface. The use of galvanised sheets was an efficient and inexpensive solution of this problem. Now that this is largely barred, other methods applicable to black sheet, such as stove-painting at the sheetmakers' works, are being evolved and will undoubtedly be more freely used in the future.

Equivalent Thicknesses of Galvanised and Black Sheets.—Finally, since there have been several cases in which serious corrosion troubles have resulted from the use of excessively thin black sheets, either through force of necessity or from a laudable desire to economise in materials, it may serve a useful purpose to tabulate, on the basis of the experimental results, the equivalent thicknesses of galvanised and black sheets, respectively, so far as resistance to atmospheric corrosion is concerned. This is done in Table XXI. It is assumed that the galvanised sheets carry 0.75 oz. of zinc per sq. ft. of surface² and that under the conditions of use mild steel corrodes 15 times as rapidly as zinc; in these circumstances the respective sheets in each pair would have the same life when exposed in the unpainted condition.³

It is clear that for equal corrosion resistance there is a considerable

¹ Khartoum can obviously be ignored in this connection.

² In practice, the coating weight would vary with the gauge.

³ The calculation assumes that the sheets are exposed to equally corrosive conditions on both sides. Under many practical conditions this would not be so, *e.g.*, roofing and side sheets, and the differential in thickness could be safely halved.

difference between the gauges of galvanised and black sheets ; 16-gauge galvanised sheet is equivalent to 12-gauge black sheet and, at the other end of the scale, 26-gauge galvanised to 17-gauge black.

If it were possible to ensure that all industrial sheeting were protected with a perfectly continuous paint coat, renewed at precisely the right time, differences in the gauge of the sheets would be of little importance as regards resistance to corrosion, but this is obviously an impracticable ideal. It is desirable that the basis steel sheet itself should be sufficiently stout to withstand

TABLE XXI.—*Equivalent Thicknesses of Galvanised and Black Sheets for Equal Resistance to Atmospheric Corrosion.*

Galvanised Sheets.		Black Sheets.	
Gauge.	In.	Gauge (approx.).	In.
16	0·064	12	0·102
18	0·048	13½	0·086
20	0·036	15	0·074
22	0·028	16	0·066
24	0·022	16½	0·060
26	0·018	17	0·056

corrosion at any exposed places for a reasonable time until the coating is renewed. In view of the high rates of corrosion observed in industrial atmospheres, it is unwise to cut down the gauge of sheeting too much, and, in general, when specifying that galvanised sheet shall be replaced by black sheet, due regard should be paid to the marked difference in the corrosion resistance of the materials and the gauge of the black sheet should be correspondingly increased ; an extra allowance of at least 0·020 in. is desirable.

APPENDIX A.—*Method of Derusting Specimens after Exposure.*

The final determination of the loss in weight of the specimens is conducted in three stages, the specimens being weighed successively (a) as received on return from exposure, (b) after as much rust as possible has been removed by scratch-brushing and finally (c) after the residual rust has been removed by treatment in an acid bath containing an inhibitor.

The process is illustrated by the detailed data given in Table XXII. It will be seen that in this case, which is typical, about 70 g. of rust remained on the specimens after exposure, of which rather less than 10 g. were removed by scratch-brushing.

The acid bath used for the final removal of the rust consists of 20% by volume of sulphuric acid to which 0·05 g. of di-*o*-tolylthiourea¹ is added to inhibit the attack on the basis metal ; it is

¹ Kindly supplied for the purpose by Imperial Chemical Industries (Dyestuffs), Ltd.

TABLE XXII.—*Typical Table of Results.*
 Sheffield. Part III. Results of the Tests on the Sand-Blasted Specimens Exposed for 5 Years.

Material.	Analysis. ¹				Specimen No.	Stand No. and Position. ²	Loss in Weight, g., after—		
	Cr. %.	Cu. %.	Mn. %.	Si. %.			Exposure.	Scratch-Brushing.	Derusting, Corrected.
Steel K . . .	0.98	0.03	0.60	0.12	231022 23 Mean	102e 100b	462 517 490	471 527 499	530 584 557
Steel L . . .	0.59	0.48	0.58	0.13	131509 10 Mean	101c 101d	511 440 476	520 456 488	579 515 547
Steel M . . .	0.60	0.50	0.89	0.15	131628 29 Mean	101b 101e	486 408 447	497 480 458	556 480 518
Steel N . . .	0.95	0.48	0.84	0.13	131816 17 Mean	101a 101f	407 313 360	416 326 371	473 390 432
Steel O . . .	0.03	0.52	1.56	0.33	131020 21 Mean	100a 102f	667 629 648	674 634 654	727 686 707
Swedish wrought iron S	Nil	0.60	Nil	0.02	221826 27 Mean	100d 102c	543 550 547	554 562 558	624 636 630
Steel X2 . . .	0.04	0.02	0.57	0.02	230420 21 Mean	100f 102a	806 828 817	815 837 826	866 894 880
Steel XK . . .	0.07	0.03	0.59	0.10	130905 06 Mean	102b 100e	739 720 730	747 729 738	801 786 794
Steel ZK . . .	0.05	0.50	0.60	0.12	131206 07 Mean	102d 100c	633 653 643	643 664 654	700 723 712

¹ The carbon content of all steels is 0.2-0.3%.
² Positions a, b and c are in the top row and d, e, f in the bottom row, in order from the left in each case as seen from the front.

heated to 40° C. Standard practice consists in immersing the specimens for 60 min., but if rusting has been severe a second immersion may prove necessary. Despite the presence of the inhibitor, there may be some slight attack on the basis metal. Corrections for this are made by conducting the derusting of selected specimens under a hood of sheet lead, which enables the hydrogen evolved to be collected; the weight of iron dissolved is calculated from this. Corrections are generally small, and for one hour's treatment in a new bath are less than 1 g. per specimen for copper-bearing materials and ingot iron, about 2 g. for ordinary steel and 5 g. for non-copper-bearing wrought irons; greater losses may occur in old baths and in cases where specimens have to be immersed a second time. Wherever possible, the materials requiring the highest corrections are derusted first in the new baths.

The final loss in weight is corrected for slight deviations from the standard dimensions to a standard size $38.1 \times 25.6 \times 0.95$ cm. ($15 \times 10.08 \times 0.374$ in.), chosen as being the general average for all materials. This corresponds to a total area, including all four edges, of 2071.8 sq. cm., or 321.1 sq. in., or 2.23 sq. ft. Values for corrosion in inches of steel or iron given in this paper have been calculated by multiplying the corrected loss in weight in grammes per specimen by 0.00002421; the factor for conversion from grammes per specimen to ounces per square foot is 0.01581.

The procedure and also the degree of reproducibility between duplicate specimens may be illustrated by a typical Table of Results (Table XXII.). Although detailed tables such as these have been omitted from the present paper, they are available in the Committee's files for all test series completed since the publication of the Fifth Report.

APPENDIX B.—*Results of Tests on Small Pollution Specimens.*

The exposure of small control specimens of ingot iron or zinc, each 4×2 in. $\times \frac{1}{8}$ in. thick (ingot iron) or $\frac{1}{16}$ in. thick (zinc), at the various exposure stations for periods of one year and, in some cases, of five years, has been continued. The specimens are exposed vertically near the tops of some of the stands used for the main specimens. The mill scale is removed from the ingot iron by pickling before exposure; the zinc is exposed with the bright as-rolled surface, after a degreasing treatment.

Synopses of the results are given in Tables XXIII. (ingot iron) and XXIV. (zinc.) These include several determinations made in the course of subsidiary series of tests conducted elsewhere than at the main stations, and some figures obtained at three representative American stations with the collaboration of the American Society for Testing Materials, and (in pre-war days) at Berlin-Dahlem with the collaboration of the Staatliche Materialprüfungsamt. Results

TABLE XXIII.—Results of Observations on Ingot-Iron Pollution Specimens ($4 \times 2 \times \frac{1}{8}$ in.).

Station.	Number of Observations.	1-Year Tests.			5-Year Tests.			Ratio of Losses, 5-Years/1-Year.	
		Loss in Weight. Mg.			Loss in Weight. Mg.	Corrosion Rate per Year.			
		Max.	Min.	Mean.		10 ⁻⁴ in.	Oz. per sq. ft.		
<i>Home.</i>									
Calshot	10	7,186	4,220	6,099	2713	1-770	18,886	1681	1-10
Dove Holes Tunnel (Up	6	9,995	5,396	7,466	3322	2-167	27,975	2490	1-62
	4	7,896	7,143	5,578	3178	2-073	32,892	2927	1-91
Llanwryd Wells	11	6,218	3,399	5,229	2326	1-517	15,739	1401	0-91
Motherwell	11	9,386	6,574	8,172	3,636	2-372	29,124	2591	1-69
Redcar ^a	(17,862) ^a	(1-04)	...
Sheffield	9	13,397	8,739	11,532	5131	3-347	49,340	4390	4-32
Woolwich	9	11,107	7,316	8,909	3964	2-585	30,245	2690	1-75
Derby North End	3	14,048	11,508	12,516	5568	3-632
Derby South End	3	13,770	11,056	12,046	5359	3-496
Farnborough ^a	20,706 ⁴	1842	1-20
Frodingham	6	23,400	10,374	14,814	6591	4-299
Sheffield University	8	11,861	8,432	9,981	4441	2-896	41,350	3679	2-40
<i>Overseas.</i>									
Abisko	6	721	335	464	206	0-135	1,216	108	0-071
Apapa	7	2,943	1,470	2,293	1020	0-665	9,133	813	0-530
Aro	7	1,530	736	1,192	530	0-346	2,968	264	0-172
Basrah	8	2,172	678	1,389	618	0-403	3,816 ⁴	253	0-185
Congella	8	11,128	5,611	7,542	3266	2-131	27,204	2421	1-58
Khartoum	9	276	49	158	70	0-046	205	18	0-012
Singapore	10	1,743	1,046	1,358	604	0-394	4,902	436	0-285
Berlin-Dahlem	3	4,828	4,547	4,708	2095	1-365
Sandy Hook, N.J.	1	7,340	3266	2-130	17,421	1550	1-01
State College, Pa.	1	3,746	1666	1-087	10,279	914	0-60
Pittsburgh, Pa.	1	9,645	4291	2-799	26,102	2323	1-51

† The mean losses in weight over 1 year used for these computations are those for the five particular yearly periods over which the 5-year specimens were exposed and differ from the mean values shown in this Table.

used and differ from the mean values shown in this Table.

This figure is not a true indication of the atmospheric pollution, as the specimens became thickly coated with iron dust on the flanges.

TABLE XXIV.—Results of Observations on Zinc Pollution Specimens ($4 \times 2 \times \frac{1}{20}$ in.).

Station.	Number of Observations.	1-Year Tests.				5-Year Tests.				Ratio of Losses, 5-Years/1-Year. ¹
		Loss in Weight, Mg.			Mean Corrosion Rate per Year.	Loss in Weight, Mg.	Corrosion Rate per Year.			
		Max.	Min.	Mean.			10-in.	Oz. per sq. ft.		
<i>Home.</i>	10	314	202	263	135	1,014	104	0.082	4.06	
Calshot	7	7206	5031	6110	3137	28,203	2896	1.726	4.40	
Dove Holes Tunnel { Up Down	5	7012	5959	6446	3310	28,867	2965	1.767	4.48	
Llanwrtyd Wells	11	344 ^a	166	239	123	930	96	0.073	3.63	
Motherwell	9	375	269	337	173	1,758	181	0.087	5.43	
Redcar ^a	(5,007) ^d	(514)	(0.306)	...	
Sheffield	9	1692	1062	1324	680	6,324	649	0.387	5.07	
Woolwich	9	339	247	292	150	1,540	158	0.094	5.62	
Derby North End	3	734	574	638	328	
Derby South End	3	605	514	555	285	
Farnborough	707 ^e	73	0.043	...	
Frodingham	2	817	779	798	410	
Sheffield University	8	674	235	446	229	2,374	244	0.145	5.14	
<i>Overseas.</i>	6	68	27	41	21	124	13	0.008	3.12	
Abisko	7	116	57	83	43	307 ^e	32	0.019	3.49	
Apapa	7	168	79	121	62	164 ^e	17	0.010	1.39	
Aro	8	141	60	84	43	167 ^e	14	0.009	1.70	
Basrah	9	415	255	311	160	1,406	144	0.086	4.23	
Congella	9	50	20	38	20	71	7	0.004	1.78	
Khartoum	9	92	26	70	36	295	30	0.018	3.54	
Singapore	10	
Berlin-Dahlem	3	231	190	211	108	
Sandy Hook, N.J.	4	228	183	203	103	880	88	0.053	4.24	
State College, Pa.	4	105	49	65	35	428	44	0.026	6.68	
Pittsburgh, Pa.	4	688	552	610	304	3,011	309	0.184	4.94	

¹ The mean losses in weight over 1 year used for these computations are those for the five particular yearly periods over which the 5-year specimens were exposed and differ from the mean values shown in the Table.

² This figure is not considered reliable, as the specimens had suffered considerable abrasion at the suspension holes (zinc wire having been used to hang them) and one had also been blown down during exposure.

^a Specimens lost.

^b One specimen only.

^c See footnote No. 3 to Table XXIII.

^d Actually exposed for 6 years.

^e Mean for 2 observations.

for individual years are not given, but are available in the Corrosion Committee's files.

In the one-year tests there are wide variations in the losses in weight for individual years; these are probably associated with variations in the meteorological conditions, including atmospheric pollution. In the five-year tests on ingot iron, the rates of corrosion are less than those for the standard $15 \times 10 \times \frac{3}{8}$ -in. specimens exposed over the same five-year period. This will be seen by comparing Tables IV. and XXIII., but it will also be evident that, with the exception of Congella, which occupies a slightly different position in the two lists, the order of corrosiveness of the experimental stations is the same for both types of specimen. The differences in the absolute rates of corrosion may legitimately be attributed to the marked difference in their respective sizes.

The figures given in the last columns of Tables XXIII. and XXIV. for the rates of the losses in weight over five years and over one year, respectively, show that for ingot iron this is less than 5 in all cases. It may be concluded that the rate of atmospheric corrosion of iron tends to slow down with increasing duration of exposure, a fact in agreement with the results of the corrosion-time tests at Sheffield and Llanwrtyd Wells (*cf.* Fig. 3). The same conclusion holds true for zinc, except in the industrial atmospheres, Sheffield, Sheffield University, Woolwich and Pittsburgh, where the rate remains approximately constant.¹

It should be added that the collection and analysis of rain water from the four main corrosion stations² was discontinued on the outbreak of war. Some additional observations, not published, are recorded in the Corrosion Committee's files.

CORRESPONDENCE

Mr. J. DEARDEN (London, Midland and Scottish Railway Company Research Laboratory, Derby) wrote: The very low rate of corrosion obtaining at such arid stations as Khartoum, Abisko and Basrah indicates that local rainfall conditions should be taken into account when assessing the losses due to atmospheric corrosion. The results from these three stations make it apparent that little or no corrosion occurred while the specimens were dry, and hence that atmospheric corrosion should alternatively be assessed on a basis of hours of rainfall at each station.

In the absence of actual recordings of this quantity, the writer has attempted an approximation based on data given in "The Climate of the British Isles" (by E. G. Bilham), Table 21, p. 112,

¹ In the case of Sandy Hook, where the ratio of the 5-year to the annual loss is 6.58, the conditions were exceptionally corrosive during the first year of the tests, and the comparison is doubtful.

² Fifth Report, *loc. cit.*, p. 63.

which shows that the average duration of rainfall in Britain lies between 17 and 25 hr. per in. of rain, and the value is independent of the total rainfall. As corrosion will continue after the cessation of rainfall until the specimen has dried, the upper limit of 25 hr. per in. has been adopted in calculating the approximate number of "wet hours" at the exposure stations. It is realised that this method is very approximate, particularly for the overseas stations, but it is considered that there must be some connection between rainfall and corrosion. The need for this is important in view of the proved variation in the rate of corrosion with time of exposure at any given station, and the author's comments on the proposal would be welcome.

Table A has been prepared on the lines indicated, using data given in Tables I. and IV. The corrosion rates have been converted into terms of grammes per square metre per "wet hour," which the writer prefers to mils per calendar year.

TABLE A.—*Rate of Corrosion (5-Year Period) expressed on an Alternative Basis.*

Station.	Annual Rainfall.		Rate of Corrosion over a 5-Year Period. G. per sq. m. per "wet hour."
	In.	Hr. (approx.).	
Sheffield	30	750	5.4
Woolwich	23	580	3.8
Redcar	25	630	3.0
Motherwell	32	800	2.6
Basrah	7	175	2.6
Calshot	26	680	2.4
Congella	43	1100	1.6
Abisko	11	270	1.0
Llanwrtyd Wells . .	55	1400	0.9
Aro	45	1100	0.4
Apapa	72	1800	0.4
Singapore	95	2400	0.2
Khartoum	6	150	0.2

On this basis the rate of corrosion at Calshot is 2.7 times that at Llanwrtyd Wells, compared with the ratio of 1.3 derived from the corresponding figures in Table IV. It would appear from this that a marine atmosphere is more corrosive than the author suggests, and that it approaches that of industrial atmospheres. The corrosion rate at Basrah now appears to be of the same order as that at the industrial stations, but in the absence of local knowledge it is not possible to draw any conclusions from this.

If reliable meteorological data concerning the duration of rainfall at each of the stations could be obtained for each year of the

exposure tests, it might be profitable to apply the suggested method to the results which have accumulated to date. Regarding future work, the recording of the duration of rainfall by suitable apparatus installed at each exposure station would appear to be necessary if concordant and significant results are to be obtained.

AUTHOR'S REPLY.

Dr. HUDSON wrote in reply: I thank Mr. Dearden for his contribution, which raises some interesting points. I hope he will forgive me if I suggest that he is confusing two distinct questions, (a) the practical interpretation of the Committee's results and (b) the correlation of the rate of atmospheric corrosion with meteorological conditions. As regards the former, there is little point in expressing the results in the form shown in the last column of his Table A, which is virtually an attempt to calculate what the corrosion rates would be at the various stations if it rained continuously at all of them. Actually an annual rainfall of 30 in. is as characteristic of Sheffield, within the possible limits of annual variation, as one of 7 in. is characteristic of Basrah, so that for practical purposes the best method of presentation is that adopted in the paper, namely, to give the results obtained in terms of the corrosion suffered per unit period of exposure. On the other hand, it may have been unwise to label the various stations as "marine atmosphere," "industrial atmosphere," &c., since these terms do not in fact fully define the conditions but merely indicate that the stations concerned are near the sea or in an industrial area, &c. Corrosion at all of them is influenced by numerous other factors, of which rainfall is undoubtedly one; consequently, considerable variation in corrosion rate is to be expected, for instance, from one "marine" atmosphere to another.

Concerning the correlation of atmospheric corrosion test results with meteorological data, I can make a more constructive reply. The problem has been studied by a number of investigators, but as regards the precise point at issue, the effect of rainfall, it will suffice to refer to the work of Schikorr in Germany, and of Schramm and Taylerson in the United States.¹ Both authorities came to negative conclusions concerning the existence of a *direct* correlation between rainfall and atmospheric corrosion. Thus, Schikorr² writes: "To investigate the relationship between atmospheric rusting and the weather condition, freshly prepared steel plates were exposed on the roof of the Staatliche Materialprüfungsamt (at

¹ G. Schikorr, *Zeitschrift für Elektrochemie*, 1936, vol. 42, p. 107; 1937, vol. 43, p. 697.

G. N. Schramm and E. S. Taylerson, American Society for Testing Materials, Mar. 7, 1934, "Symposium on the Outdoor Weathering of Metals and Metallic Coatings," p. 51.

² G. Schikorr, *Zeitschrift für Elektrochemie*, 1936, vol. 42, p. 113.

Berlin) during each month throughout the period from November, 1933, to December, 1935. No simple correlation was found between the extent to which they had rusted and the (monthly) rainfall, but on the other hand a parallel relationship was observed between the rate of rusting and the average relative humidity. . . . This parallelism is attributable to the following factors: (1) Both variables are markedly dependent upon the duration of rainfall; (2) at relative humidities above 70% rusting can occur in the absence of liquid water ('dry rusting'); (3) during the winter months the average relative humidity varies in a similar manner to the sulphuric acid content of the atmosphere (both increasing as the temperature falls)."

Schramm and Taylerson¹ state: "There is no direct relationship between the amount of rainfall and the amount of corrosion of commercial irons and steels during a period of one year. . . . A

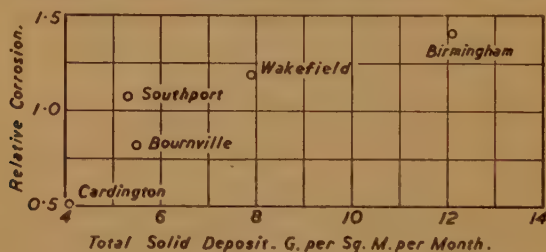


FIG. A.—Relation between Corrosion and Atmospheric Pollution. Non-ferrous metals.

relationship between air pollution, as measured by fuel consumption in the neighbourhood, and corrosion was found to exist in two instances."

Briefly, then, the two main factors determining atmospheric corrosion are the atmospheric pollution and the atmospheric humidity, which is dependent on the rainfall. Judging from the results of Vernon's fundamental laboratory researches² and of my own field tests, on both non-ferrous and ferrous metals, I attach the greater influence to the former. This may be illustrated by the data shown in Figs. A and B, respectively. Fig. A is based on the results of the field tests on fully exposed specimens of twelve non-ferrous metals and alloys that I conducted on behalf of the British Non-Ferrous Metals Research Association.³ The mean corrosion rate of these materials is plotted against the atmospheric pollution, as determined by collecting the rain water in a suitable gauge and analysing it at intervals. Fig. B is a similar graph referring to the

¹ G. N. Schramm and E. S. Taylerson, *loc. cit.*, synopsis at head of paper.

² W. H. J. Vernon, *Transactions of the Faraday Society*, 1931, vol. 27, pp. 255, 582; 1935, vol. 31, p. 668, and other publications.

³ J. C. Hudson, *Transactions of the Faraday Society*, 1929, vol. 25, p. 242.

rate of rusting of ordinary mild steel as observed in the present tests at the four main stations of the Corrosion Committee.

The general parallelism between atmospheric pollution and corrosion is evident in both cases. Clearly there is no exact correlation, but it is also clear that atmospheric pollution itself cannot be assessed as a single entity—a statement of the total deposit of solids in a given period is far from defining it completely, and, moreover, as already stated, other factors come into play. Incidentally, it may be noted that Mr. Dearden's conception of corrosion rate per rainfall-hour does help to reduce a discrepancy in the

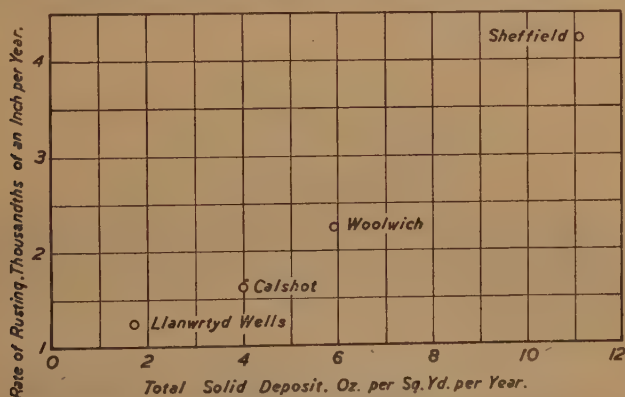


FIG. B.—Relation between Rate of Rusting and Atmospheric Pollution. Mild steel.

results for the ferrous metals (Fig. B). Here the rate of corrosion in the rural atmosphere of Llanwrtyd Wells is greater than would be expected from the atmospheric pollution. The rainfall at this station is, however, 55 in. per annum, as compared with 23–30 in. at the other stations. If the results are expressed in grammes per square metre per “wet hour,” as Mr. Dearden suggests, the points for Llanwrtyd Wells, Calshot and Woolwich are found to lie almost exactly on a straight line, although the point for Sheffield now falls below the line.

It is an interesting speculation whether some simple correlation between rusting, rainfall and atmospheric pollution may not exist, say in the form $R = W(a + bP)$, where R is the rate of rusting, W the rainfall and P the atmospheric pollution, a and b being constants. The matter could be investigated by conducting tests in the neighbourhood of pollution gauges, such as those used at numerous stations in this country by the Advisory Committee on Atmospheric Pollution of the Department of Scientific and Industrial Research. Perhaps when normal times return something may be attempted on these lines.

THE BRITTLE CONSTITUENT OF THE IRON-CHROMIUM SYSTEM (SIGMA PHASE).

I.—A SURVEY OF THE LIMITS OF THE SIGMA PHASE IN THE BINARY SYSTEM.*

BY A. J. COOK AND F. W. JONES, PH.D.

(Under the direction of Dr. C. Sykes, F.R.S., Superintendent, Metallurgy Department, National Physical Laboratory, Teddington.)

(Figs. 2 to 10 = Plates XII. and XIII.)

Paper No. 11/1943 of the Alloy Steels Research Committee (submitted by Dr. C. Sykes, F.R.S.)

SYNOPSIS.

The existence of a second phase in the binary iron-chromium system has been confirmed and the phase boundaries have been established down to a temperature of 600° C. X-ray powder photographs have been used to identify the phases after annealing filings and solid samples at various temperatures.

A marked feature of the phase is a very slow rate of reaction near its upper temperature limits, which it is considered is due to true hysteresis.

The presence of cold-work has been found to have an accelerating effect on the rate at which the σ constituent can be produced in the alloys. Microphotographs are shown of partial and complete transformation from the α to the σ phase.

Introduction.

ALTHOUGH several previous workers have stated that the binary alloys of iron and chromium do not form a continuous series of solid solutions, but over a considerable range of composition produce a second phase identified as the σ phase, it is only recently that there has been wider acceptance of this view. The possibility of the formation of the σ phase, which is stated to be very brittle, may be of considerable importance in connection with the industrial application of certain heat-resistant alloys containing iron and chromium. On this account the present work was commenced at the request of the Alloy Steels Research Committee to investigate the phase boundaries of this constituent in iron-chromium alloys of high purity.

Early experiments with the alloys of this type made by Adcock ⁽¹⁾ at the time of his work on the iron-chromium constitutional diagram

* Received April 29, 1943. This paper is published by authority of the Alloy Steels Research Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

led him to believe that with high-purity alloys a second phase was not produced. Further work by Jette and Foote⁽²⁾ on the iron-chromium-silicon system gave evidence of a brittle non-magnetic phase even with an alloy containing as little as 0.087% of silicon. These investigators concluded that its rate of formation under optimum heat-treatment conditions was extremely slow in fully annealed high-purity iron-chromium alloys, but was greatly accelerated by an impurity or cold-working prior to heat treatment within the critical temperature range. Other workers on ternary systems^(3, 4, 5) have reported the presence of a σ phase which forms readily within certain ranges of composition when elements such as manganese or silicon are present even in small quantities.

Preparation of the Specimens.

A number of binary alloys of high purity made by Adcock were available in the form of solid specimens, which had been vacuum-annealed at 1300° C. for 12 hr. Full details of the preparation and purity of the materials used are given in Adcock's original paper.⁽¹⁾ Filings were taken from these alloys for this investigation, in which the powder method of X-ray technique was used in conjunction with the microscopic examination of solid samples.

Since it was intended to carry out all annealings with the powders sealed in evacuated silica capsules, a preliminary experiment was made to ensure that contamination would not occur with powders under these conditions. Two samples of a 70% chromium alloy were separately sealed in silica capsules evacuated to a pressure of the order 10^{-4} mm. of mercury. One lot of filings was carried on a piece of sintered alumina inside the silica container, the other was in direct contact with the silica. Both samples were annealed for 4 days at 1000° C. and compared spectrographically with an untreated lot; no evidence of increase in silicon content or other contamination was obtained, both samples remaining untarnished.

A controlled electric furnace was used for all heat treatments. Samples after heat treatment were not quenched in water, as it was considered that sufficiently rapid cooling was obtained by quickly withdrawing the very small specimens from the furnace tube and allowing them to cool in air. This procedure minimised the risk of breakage of the capsules.

X-Ray Investigation.

Exploratory experiments were made with filings from two alloys in the region 40–50% chromium * to determine how readily equilibrium at 600° C. could be attained with heavily cold-worked material. Each of these samples gave a new diffraction pattern after 5 days; one of composition 44.2% chromium did not retain

* The composition is expressed throughout as an atomic-percentage of chromium.

any α phase pattern, while the other with 50.5% of chromium still gave a trace of the original lines. A further 5 days failed to alter the spectrum of these samples, and it was concluded that stability in this region could be achieved in 5 days. Subsequently both of these alloys were restored to the α condition after annealing at 850° C. for 2 days. A series of six alloys ranging from 44.2% to 56.1% of chromium were annealed at 900° C. for 5 days without any change in their X-ray spectrum, thus indicating that the peak of the proposed σ loop was definitely below this temperature.

The Phase Diagram.

Filings from thirteen alloys covering the range of composition from 25% to 76% of chromium were annealed at 600° C. for periods varying from one day to 60 days. The resulting structures were identified by X-ray examination and are shown diagrammatically in Fig. 1. No change in the relative proportions of the phases

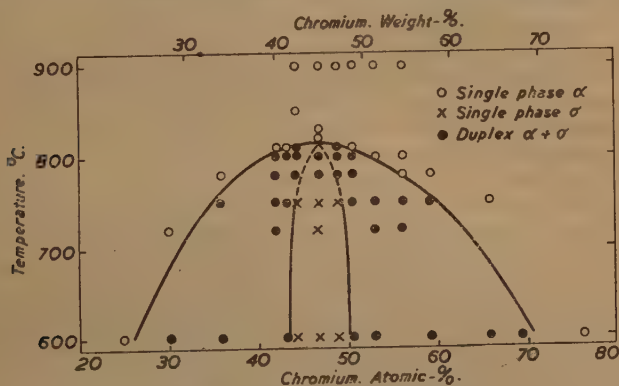


FIG. 1.—Iron-Chromium Phase Diagram over the Range 25–76% Chromium.

occurred when the annealing time was prolonged beyond 20 days with alloys near the above limits of composition, and it was assumed, therefore, that equilibrium was attained at the end of this period of annealing.

The phase boundaries for the temperature interval 600–750° C. given in Fig. 1 were finally fixed by estimating, from the relative intensity of the lines of the phases on the X-ray powder diagram, the amount of σ phase present in the two-phase alloys. They are considered to have a probable accuracy of about $\pm 1\%$.

Fig. 2 shows two typical X-ray diagrams, one of an alloy in the α phase and the other of the same alloy in the σ phase.

Hysteresis.

Above 750° C. and below 830° C. considerable difficulty was encountered in obtaining equilibrium in alloys ranging from 43%

to 50% of chromium, owing to the extremely sluggish character of the transformation. The following experimental results illustrate this peculiarity of the alloys.

Three specimens of an alloy containing 46.8% of chromium were prepared, one as pure α phase, one as pure σ phase and the third as $\alpha + \sigma$. The three specimens were then annealed for 17 days at 800° C., but no change could be detected in their structure after this treatment. A similar result was obtained on heat-treating similar specimens for 7 days at 780° C. and 26 days at 810° C.

At 820° C., however, the transformation proceeds reasonably quickly, since two further specimens of this alloy, one as pure σ and the other as $\alpha + \sigma$ annealed for 7 days, were found to consist of a two-phase structure of comparable phase proportions. Finally, a 24 days' treatment at 820° C. left the 46.8% chromium alloy as pure α , irrespective of whether the original structure was α or σ , and consequently it is concluded that the upper limit of the σ phase boundary is below 820° C. Above this temperature the reaction speed is again considerably higher, pure σ phase from an alloy of the same composition yielding pure α after 11 days at 830° C., whilst an adjacent σ alloy containing 48.8% of chromium gave a 95% α structure after only 1 hr. at 840° C.

As annealing treatments lasting about 25 days failed to bring about equilibrium in the temperature range 780–810° C. in alloys containing 46–50% of chromium, whereas equilibrium was obtained in some of the same alloys in 5 days at 600° C., i.e., at a lower temperature, it seems reasonable to conclude that there is some hysteresis effect which becomes particularly effective in such alloys in the temperature range 780–810° C. The fact that either the α or the σ phase can exist for such long periods without any noticeable change suggests that this is a case of true hysteresis and is not merely due to a very high "time of relaxation"; there is, therefore, very little possibility of accurately establishing the phase boundaries in this temperature interval and in Fig. 1 the approximate boundaries have been left dotted. The uncertainty is not likely to be large, since the alloys within the ranges 36–43% and 50.5–59% of chromium did not show any marked hysteresis. (The results plotted in Fig. 1 at 810° C. were obtained on alloys previously prepared to be in equilibrium at 750° C., those recorded at 800° C. on alloys initially in the pure α phase.)

The Effect of Cold-Work.

The rate of transformation in the temperature range 600–750° C. was very much higher in filings than in lumps. Thus, powder of an alloy containing 53% of chromium reached equilibrium as a two-phase system in 2 days at 720° C., whereas the bulk material had not started to transform after 37 days at the same temperature. Transformation in the bulk material was markedly accelerated by hammering, and local effects were produced at sawn surfaces.

SIGMA PHASE IN HIGH-PURITY IRON-CHROMIUM ALLOYS.

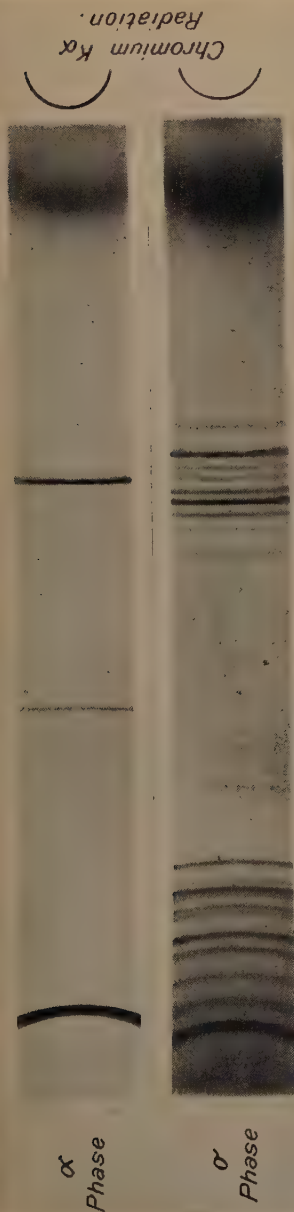


FIG. 2.—X-Ray Powder Diagrams from a 48.8% Chromium Alloy.



FIG. 3.—48.8% Chromium, annealed for 24 days at 620° C. $\times 250$.



FIG. 4.—48.8% Chromium, annealed for 24 days at 620° C., held for 4 hr. at 950° C. and quenched. $\times 250$.

(Specimens etched electrolytically in Vilella's reagent.)
(Micrographs reduced to two-thirds linear in reproduction.)

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PLATE XIII.

SIGMA PHASE IN HIGH-PURITY IRON-CHROMIUM ALLOYS.

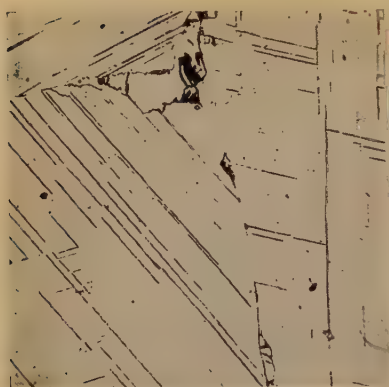


FIG. 5.—50.5% Chromium, annealed for 23 days at 620° C. $\times 150$.

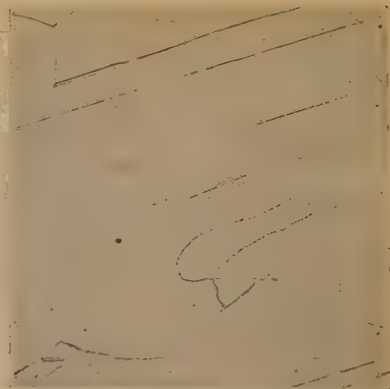


FIG. 6.—50.5% Chromium, annealed for 23 days at 620° C., held for 4 hr. at 950° C. and quenched. $\times 250$.



FIG. 7.—46.8% Chromium, annealed for 35 days at 720° C. $\times 150$.

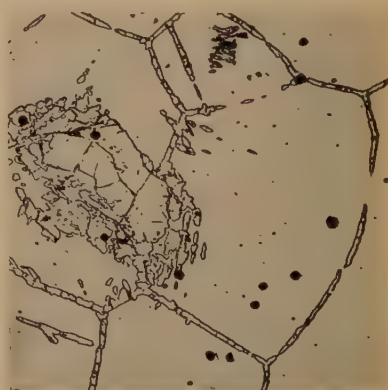


FIG. 8.—56.1% Chromium, annealed for 35 days at 720° C. $\times 75$.



FIG. 9.—42.0% Chromium, annealed for 8 days at 720° C. $\times 150$.

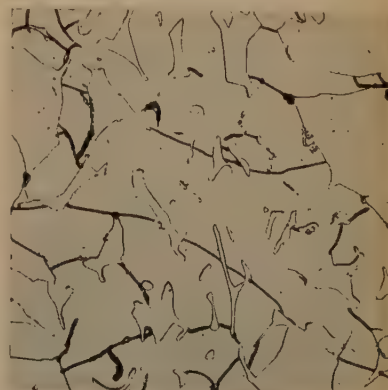


FIG. 10.—42.0% Chromium, annealed for 8 days at 720° C. $\times 500$.

(Specimens etched electrolytically in Vilella's reagent.)
(Micrographs reduced to two-thirds linear in reproduction.)

The presence or otherwise of cold-work did not eliminate the hysteresis effects already described in the previous section.

Microscopic Examination.

In addition to the X-ray work carried out with filings, some experiments were made to develop the σ phase in samples suitable for microscopic examination. Figs. 3 and 7 show the typical microstructures of alloys lying in the single-phase σ area. These specimens were non-magnetic when tested with a permanent magnet, and on attempting to polish them considerable trouble was experienced owing to their friable nature, the surfaces developing large fissures and holes. The structure in Fig. 3 was obtained by subjecting a lump of fully-annealed alloy (48.8% of chromium) to cold-work and then annealing at 620° C. for 24 days. An X-ray photograph taken with particles crushed from this sample showed no lines of the α phase. A duplicate solid sample heat-treated similarly was completely converted back to the α state, as illustrated in Fig. 4, by quenching after a short annealing at 950° C.

In order to ascertain the mode of formation of the σ phase other samples were annealed for further periods and examined immediately. A cold-worked sample of the 50.5% chromium alloy was annealed at 620° C. for one day without any change in the X-ray spectrum or microstructure other than the development of criss-cross markings which it was finally concluded were due to strain induced by the preliminary cold-working. The annealing of this specimen at 620° C. was continued for a period of 5 days without producing any change in structure, but after another 17 days traces of a boundary constituent were found, as shown in Fig. 5. This quantity of second phase was insufficient to give fresh lines on the X-ray diagram. The 48.8% alloy transformed very much more rapidly than the 50.5% alloy. The strain markings persisted throughout the worked samples annealed at low temperatures, and a period of 8 hr. at 950° C. did not bring about their complete removal (Fig. 6), although a shorter period at 1150° C. was effective.

In a further treatment the strain-line effects were avoided by annealing without any initial cold-work other than that occasioned by sawing the specimens. Fig. 7 illustrates the single-phase σ alloy (46.8% of chromium) obtained after a 5 weeks' annealing treatment at 720° C., whilst Fig. 8 shows the microstructure of an alloy situated in the two-phase region. These experiments indicated that the σ network developed along the original α grain boundaries, although separate patches occasionally appeared in the body of the grains. Once this nucleus network had formed it seemed that transition to σ continued in a random manner in the interior of the grains, small islands of α remaining in the two-phase samples. This is illustrated in Figs. 9 and 10, which show the fissured σ constituent surrounding many small uncracked areas. These struc-

tures were developed after annealing a strained alloy (42.0% of chromium) for only 8 days at 720° C.; at this temperature the strain lines had almost disappeared. When filings were being taken from this latter sample for the confirmatory X-ray evidence, lustrous flakes broke away in addition to the fine particles usually obtained. These flakes were easily separated with a magnet from the finer material and gave only σ lines on the X-ray pattern. On the other hand, another alloy close in composition to the above showed relatively small quantities of the σ network after undergoing the same treatment. This difference suggested that the incidence of σ in a reasonably short time was rather fortuitous and depended on the degree of localised cold-work present in various parts of the alloys before annealing.

It will be clear from the above description that the difficulties encountered in obtaining equilibrium with powders are very much accentuated in the material in bulk form, since the rate of approach to equilibrium varies very considerably from specimen to specimen, depending on its previous mechanical treatment.

Iron-chromium alloys which contained σ phase did not exhibit the same passivity to etching reagents which was such a marked feature of the original alloys annealed at high temperatures (1200–1300° C.). It was possible to develop the structures illustrated by electrolytic etching alone in Vilella's reagent; times of the order of 20 sec. were found sufficient. Samples which had been heavily cold-worked were found to etch without electrolysis independently of the presence of σ constituent.

Summary and Discussion.

In the pure binary alloys the α phase is the stable phase above 820° C. At temperatures below this the σ phase appears in the region of 50% of chromium, the probable phase boundaries being indicated in Fig. 1. At 600° C. the σ phase is likely to be present in alloys containing from 26% to 71% of chromium, a range of composition much wider than that reported by previous workers.⁽⁶⁾ The alloys are pure σ phase from 44% to 50% of chromium.

The rate of approach to equilibrium is quite slow in bulk material, but may be accelerated by cold-working. In the temperature range 770–820° C. a hysteresis effect appears to exist in certain alloys containing somewhat less than 50% of chromium and the final structure of these alloys is unlikely to change from the initial structure for very long periods of time when heated within this temperature range.

The present investigation was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of the Alloy Steels Research Committee, and is published by permission of the Director of the Laboratory.

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- (4) BURGESS and FORGENG : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1938, *Iron and Steel Division*, vol. 131, p. 291.
- (5) BRADLEY and GOLDSCHMIDT : *Journal of The Iron and Steel Institute*, 1941, No. II., p. 273P.
- (6) WEVER and JELLINGHAUS : *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1931, vol. 13, p. 143.

CORRESPONDENCE.

Mr. H. J. GOLDSCHMIDT (Messrs. William Jessop & Sons, Ltd., Sheffield) wrote : I should like to congratulate the authors on their admirable paper, which goes far to clear up the difficulties left by earlier investigations.

It is surprising that Adcock¹ and Preston, who examined the same alloys by X-rays, failed to find the σ phase, even after annealing the 48.8% and 50.5% chromium alloys at 600° C. for 4 days, the reason evidently lying in the sluggish behaviour of the alloys. However, Preston's lattice-spacing curve (Fig. 13 in Adcock's paper¹) shows a flattening and an inversion around 40% and 50% chromium, which suggests a connection with the σ phase, possibly due to superlattice formation.

The great difficulties in establishing equilibrium described by the authors were also experienced by Dr. A. J. Bradley, F.R.S., and myself some years ago at Manchester. In review some of these results well support the present conclusions, though in the light of the present work they suffered from the hysteresis effect. However, I think a brief comparison may be of interest.

On a series of binary alloys the following phase constitutions were obtained after annealing the lumps at 1200° C. for 3 days and "slow cooling" from 900° C. approximately at a rate of 10–20° C. per hr. (identical heat treatment for all alloys) :

0%, 25%, 40% chromium : α single phase.
 42%, 45%, 47.5% chromium : $\alpha + \sigma$.
 50% chromium : σ .
 52%, 55%, 57% chromium : $\sigma + \alpha$.
 60% chromium : α single phase.

The rate of cooling was such that, according to Cook and Jones' diagram, the equilibrium attained would correspond to approximately 760–790° C. The fact that under these conditions it was possible to obtain the 50% chromium alloy as pure σ would suggest

¹ *Journal of The Iron and Steel Institute*, 1931, No. II., p. 147.

placing the dotted upper boundary of the σ region with a bias towards the chromium side.

A number of experiments have been made with the 50/50 Fe-Cr alloy. These suggested that the $\alpha/(\sigma + \alpha)$ change point lies somewhat above 830°C ., but well below 1000°C . The alloy, when water-quenched from 830°C . after annealing for 2 hr. (previous lump-anneal at 1300°C . for 21 days), still yielded $\sigma + \alpha$; when the powder was slowly cooled, instead of quenched, pure σ was obtained. Generally the conditions for the formation of σ seemed to depend on the rate of entry into the σ field, being more favourable when the alloy was taken into the duplex or σ field slowly from a higher temperature.

The hysteresis effect may be demonstrated in a different manner by the following series of observations; powders originally in the α state had been quenched from a series of temperatures between 1000° and 420°C ., with the following results :

Lump-anneal: 1200°C ., 3 days.

Temp. of Quench. $^\circ\text{C}$.		Constitution.	
1000	After soak for approx. 20 hr.	α	\downarrow \uparrow σ increasing.
970		α } Trace σ .	
900		α }	
850		$\alpha + \text{small } \sigma$.	
810		$\alpha + \text{medium } \sigma$.	
720		$\sigma + \text{small } \alpha$.	
650		$\sigma + \text{small } \alpha$.	
575	After soak for approx. 45 hr.	$\sigma + \text{small } \alpha$.	
420		α (diffuse reflections).	

Thus, for a given soaking time the amount of σ phase increases in the same range (850 – 720°C .) in which the authors had found the pronounced hysteresis (830 – 750°C .); the apparent maximum at 720°C . is probably due to the fact that at lower temperatures increasing sluggishness of reaction again favours the preservation of the α state. (The trace of σ phase observed even above 850°C . may have been produced during cooling, the quench not being rapid enough to suppress its formation.)

If cold-work has the effect of accelerating the transformation, the question arises whether the method of preparing powders should not be standardised, as accidental differences in filing may influence the results, even after heat treatment. Do the authors suggest that cold-work alone was responsible for the fact that filings reached equilibrium more quickly than lumps between 600° and 750°C .? Another reason may be that in bulk samples the transformation is inhibited by inability to undergo volume changes, so that internal stresses are produced, as is often the case with γ - α changes in steel. Incidentally, the authors' observation is also valuable in proving that for the determination of equilibrium diagrams involving the σ phase, the powder method offers decided advantages over those relying on bulk samples (*e.g.*, microscopic).

It is hoped that the authors will extend the work to ternary systems involving nickel, manganese and silicon, and in particular verify the effect of nickel, which greatly widens the regions of stability of σ . The present α - σ hysteresis phenomena seem to have certain features in common with the γ - α ones in the Fe-Ni system, and it may be noted that the 18/8-type steels are situated in an area of the Fe-Cr-Ni ternary system where the sluggish γ - α change is not far from giving way to the $\gamma(\alpha)$ - σ change. The chief practical importance of the paper probably lies in this fact.

In conclusion, may I enquire whether, in the authors' opinion, the change from the α to the σ lattice occurs spontaneously? Some of our results suggested, though not conclusively, the existence of an intermediate stage between the two phases, which manifests itself by certain lines (not due to σ) additional to the body-centred cubic pattern, and which appear just before the precipitation of σ . Superlattice formation or another transition stage is not impossible, and I should appreciate knowing whether the authors have found any such indications.

Mr. C. O. BURGESS (Union Carbide and Carbon Research Laboratories, Niagara Falls, New York, U.S.A.) wrote: The authors are to be commended on their efforts to define more accurately the boundaries of the σ phase in pure iron-chromium alloys. In particular, their work serves to clear up the confusion following Adcock's original conclusion that a second phase is not formed in high-purity alloys. However, one statement of the authors, *i.e.*, that at 600° C. σ phase is likely to be present in alloys containing as little as 26% of chromium, should not be passed over without discussion. The minimum chromium percentage for σ formation is of considerable practical importance in view of the general use of iron-chromium alloys in the range of 20-30% chromium. In our own investigations covering "bulk" alloys of commercial purity containing 16% to 58% of chromium we have not been able to detect σ phase formation in commercial alloys with under 35% of chromium. Even at this relatively high chromium level no σ phase could be detected after 130 hr. at 600° C., and only 1-2% was present after 284 hr. at 700° C. The next lower chromium alloy containing 31.35% of chromium did not exhibit any σ phase detectable by either metallographic or X-ray diffraction methods. However, in view of the possibility that traces of the σ phase might form in submicroscopic amounts or that formation of this phase might occur at a critical temperature only after more extended exposure periods than those employed in our tests, the minimum chromium percentage for σ formation was set at 30%. It is interesting that, according to the authors' Fig. 1, traces of σ phase were actually detected in an alloy containing 30% of chromium, and it would be of interest to learn whether such formation was limited to cold-worked chips as opposed to bulk specimens.

Despite the reported formation of σ in an alloy with 30% of chromium, it is felt that further extension of the zone of σ formation to alloys containing as little as 26% of chromium, as stated in the authors' conclusions and as indicated in Fig. 1, is not justified in the absence of experimental proof. Iron-chromium alloys containing up to 30% of chromium have been extensively used in practice, and to our knowledge no evidence of σ formation has been recorded. If such a phase does form in these alloys it must certainly be in amounts so small as not to affect appreciably the properties of the alloys.

AUTHORS' REPLY.

The AUTHORS wrote in reply : We thank Mr. Goldschmidt and Mr. Burgess for their remarks, and are interested to hear that Mr. Goldschmidt's results confirm the hysteresis effect.

We consider that the method of preparation of powders would be difficult to standardise. Variations in the method of preparation should not affect the equilibrium diagram but merely the rate of approach to equilibrium. The transformation in bulk samples may be inhibited to some extent by internal stresses, but there is no doubt that the transformation proceeds much more rapidly in a cold-worked bulk sample than in an annealed one.

No evidence was found of an intermediate stage in the $\alpha \rightarrow \sigma$ transformation.

In reply to Mr. Burgess, the evidence for placing the $\alpha/(\alpha + \sigma)$ boundary at 26% chromium at 600° C. was obtained from X-ray results on cold-worked filings. After 20 days at 600° C. it was estimated, from the intensities of the X-ray lines, that the alloy of composition 30% chromium contained 25% of the σ phase. The $\alpha/(\alpha + \sigma)$ boundary should therefore be at about 26% chromium. The difference between our results and those of Mr. Burgess is probably due to the difficulty of attaining equilibrium with bulk samples.

NOTE ON SOME PRECIPITATION EFFECTS OBSERVED IN MILD-STEEL AND WROUGHT-IRON PIPE.*

BY T. H. SCHOFIELD, M.Sc.

(Under the direction of Dr. C. Sykes, F.R.S., Superintendent,
Metallurgy Department, National Physical Laboratory.)

(Figs. 1 to 12 = Plates XIV. and XV.)

SUMMARY.

Precipitates observed in mild-steel and wrought-iron pipe after service have been removed by heating at 500–520° C. and reprecipitated by prolonged heating at 150–180° C. It is probable that the precipitates consist mainly of iron nitride.

Introduction.

DURING the course of a microscopical examination of a piece of corroded mild-steel hot-water pipe (steel *CRL* in Table I.) which had been in service for about three years it was observed that the material etched in alcoholic nitric acid showed a precipitate within the grains, the amount of which varied in individual grains and sometimes seemed to bear some relation to the crystallographic planes (*cf.* Figs. 1 and 2). Much of the precipitate was very fine, but some was in the form of needles resembling iron nitride (Fig. 2). Similar precipitates were observed in samples of mild-steel and wrought-iron pipes (*A* and *C*, respectively, in Table I.) which had been recovered from a burnt building (Figs. 5 and 6). As these structures may be of general interest the following brief description is given.

Chemical Analysis.

The chemical analyses of the three materials and of a specimen of hot-rolled mild-steel plate (*GUF*) of higher carbon content than the other materials are given in Table I.; the latter steel was included in the experiments because it contained an appreciable amount of nitrogen but showed no precipitate.

TABLE I.—*Chemical Analyses of the Materials.*

Mark.	C. %.	Si. %.	S. ' %.	P. %.	Mn. %.	N. %.	Ni. %.	Cr. %.	Cu. %.
<i>CRL</i> .	0.05	0.008	0.027	0.093	0.36	0.017
<i>A</i> .	0.08	0.01	0.068	0.097	0.33	0.014
<i>C</i> .	0.05	0.13	0.026	0.31	0.04	0.008
<i>GUF</i> .	0.20	0.02	0.023	0.011	0.56	0.01	0.16	Trace	0.10

* Received May 17, 1943.

The analyses suggest that *CRL* and *A* are rimming steels, probably produced by the Bessemer process, and that *C* is a wrought iron; the steel *GUF* was known to have been produced in a basic electric furnace.

Heat Treatment and Microstructure.

On heating a small specimen of steel *CRL* for $\frac{1}{2}$ hr. at 500° C. followed by air-cooling, the precipitate almost disappeared, except for a few of the larger needles in some isolated areas. No precipitate or needles remained after heating for 18 hr. at 500° C. followed by air-cooling (Fig. 3). Similarly, no precipitate remained in specimens of *A* and *C* after heating for 18 hr. at 520° C. followed by air-cooling (Figs. 7 and 8). Because the specimen *GUF* showed no precipitate it was not heated at 500–520° C.

Attempts were then made to reproduce the precipitates by heating at low temperatures (150–180° C.). After heating specimens of *CRL* and *GUF* (*CRL* previously heated at 500° C.) for 9 days at 150° C. no precipitate was observed in either specimen. The temperature was raised to 180° C. and after 9 days some needle-like precipitate was observed in *CRL* but not in *GUF*. These two specimens together with specimens *A* and *C* (previously heated to 520° C.) were then heated for longer periods at 180° C. and examined at intervals. No further change in the amount of precipitate was observed after heating specimens *CRL*, *A* and *C* for about 35 days and no traces of precipitate were found in steel *GUF* after heating for 74 days, when the experiments were stopped.

Fig. 4 shows the structure of *CRL* after reheating for 9 days at 150° C. and 19 days at 180° C., and Figs. 9 to 12 illustrate the structures of *A*, *C* and *GUF* after heating for 74 days at 180° C. In addition to the needle-like precipitate in the wrought-iron specimen *C*, a sub-boundary precipitate, probably due to another constituent, was observed in some areas (Fig. 11).

Summary and Conclusions.

Precipitates observed in certain mild-steel and wrought-iron pipes after service have been removed by heating at 500–520° C. and reprecipitated by prolonged heating at 150–180° C.

Compounds of elements present or likely to be present in the materials which might be expected to give such precipitation effects, as judged by the form of their solubility curves in ferrite, are iron carbide, iron nitride and possibly iron phosphide. The needle-like habit of the precipitate suggests that it may be iron nitride. If this is true, whether precipitation occurs or not after low-temperature heating appears to depend on the composition and/or the initial condition of the material as well as on the nitrogen content, since the steel *GUF*, containing 0.01% of nitrogen, gives no precipitate after a period of heating in which the wrought-iron tube *C*, con-

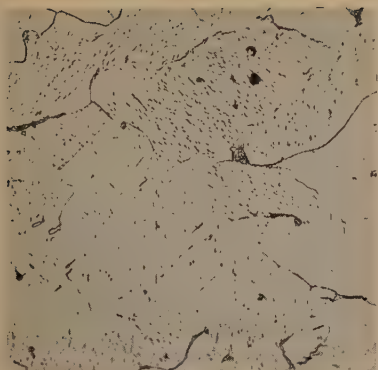


FIG. 1.—Mild-Steel Pipe CRL, as received. $\times 500$.



FIG. 2.—Mild-Steel Pipe CRL, as received. Field not included in Fig. 1. $\times 1500$.

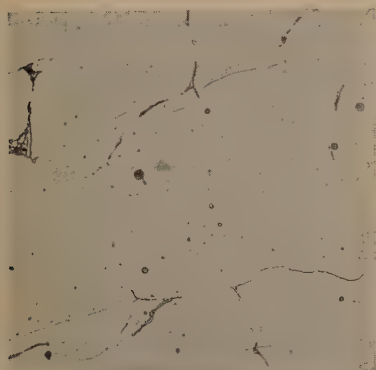


FIG. 3.—Mild-Steel Pipe CRL, heated for 18 hr. at 500°C ., air-cooled. $\times 500$.

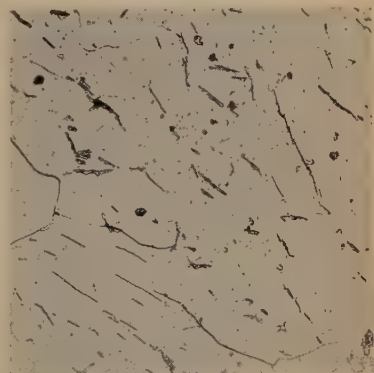


FIG. 4.—Mild-Steel Pipe CRL, heated for 18 hr. at 500°C ., air-cooled, held for 9 days at 150°C ., followed by 19 days at 180°C . $\times 500$.

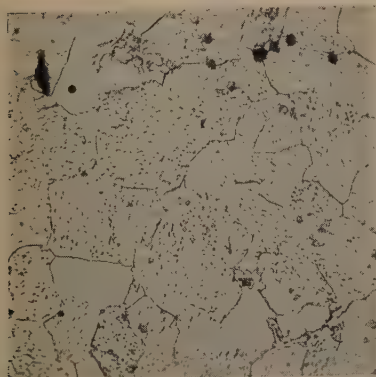


FIG. 5.—Mild-Steel Pipe A, as received. $\times 500$.

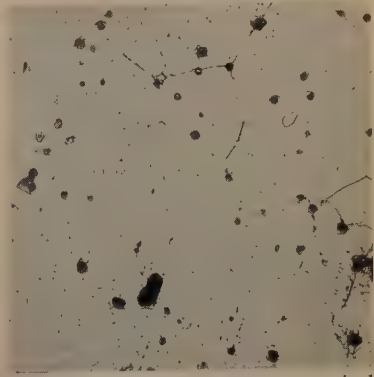


FIG. 6.—Wrought-Iron Pipe C, as received. $\times 500$.

All specimens etched in a solution of nitric acid in alcohol.
(Micrographs reduced to two-thirds linear in reproduction.)

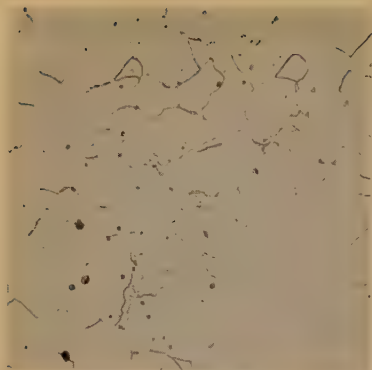


FIG. 7.—Mild-Steel Pipe A, heated for 18 hr. at 520° C., air-cooled. $\times 500$.



FIG. 8.—Wrought-Iron Pipe C, heated for 18 hr. at 520° C., air-cooled. $\times 500$.



FIG. 9.—Mild-Steel Pipe A, heated for 18 hr. at 520° C., air-cooled, then reheated for 74 days at 180° C. $\times 500$.

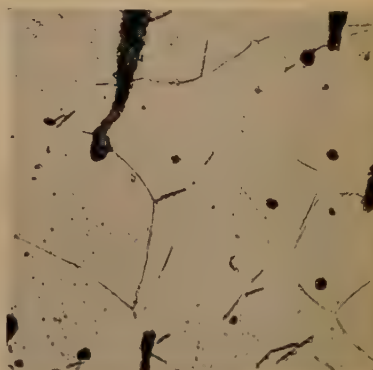


FIG. 10.—Wrought-Iron Pipe C, heated for 18 hr. at 520° C., air-cooled, then reheated for 74 days at 180° C. $\times 500$.

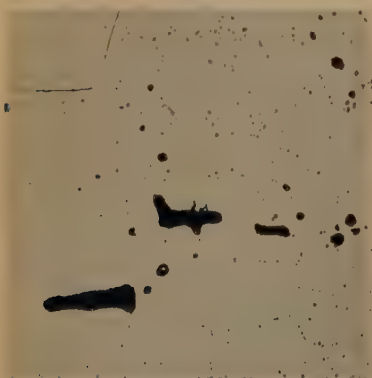


FIG. 11.—Wrought-Iron Pipe C, heated for 18 hr. at 520° C., air-cooled, then reheated for 74 days at 180° C. $\times 500$.

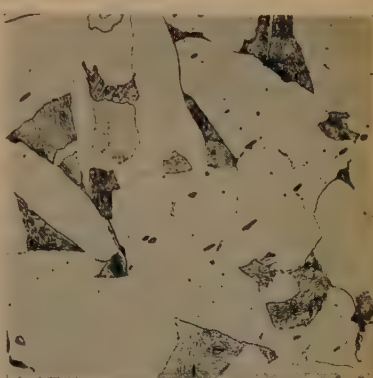


FIG. 12.—Plate Steel GUF, heated for 74 days at 180° C. $\times 500$.

All specimens etched in a solution of nitric acid in alcohol.
(Micrographs reduced to two-thirds linear in reproduction.)

taining 0.008% of nitrogen, does so. In this connection it is noteworthy that the materials showing the precipitate have also a high phosphorus content.

Dean, Day and Gregg,⁽¹⁾ Köster⁽²⁾ and Epstein⁽³⁾ have noted similar precipitation effects in iron and mild steel. The former workers observed that high-purity electrolytic iron normally showed no needles, but when melted in air or melted in vacuum and treated with ammonia needles of a type similar to those illustrated here appeared.

It is probable that the precipitate was not present in the pipes before service, but was produced by prolonged heating at temperatures near 100° C., and at this temperature the precipitate is finer than that produced at 150–180° C.; a sub-boundary precipitate observed in the wrought-iron specimen in addition to the needle form may be due to another constituent.

The work described above was carried out as part of the research programme of the National Physical Laboratory and the paper is published by permission of the Director of the Laboratory.

REFERENCES.

- (1) DEAN, DAY and GREGG : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1929, vol. 84, p. 446.
- (2) KÖSTER : *Archiv für das Eisenhüttenwesen*, 1930, vol. 3, p. 647.
- (3) EPSTEIN : *Proceedings of the American Society for Testing Materials*, 1932, vol. 32, Part II., p. 293.

CORRESPONDENCE.

Mr. C. DINSDALE (London and North-Eastern Railway Company, Doncaster) wrote : The identity and formation of the needles described by Mr. Schofield was the subject of a special article entitled "The Embrittlement of Wrought Iron in Service and the Development of Needles therein," which appeared on pp. 91–99 of the *Technical Report for 1932* issued by the British Engine Boiler and Electrical Insurance Co., Ltd.

From microscopical and other evidence it was suggested that these needles, which were formed in certain grades of wrought iron in parts working with saturated steam at a pressure between, say, 100 and 200 lb. per sq. in. or at an equivalent temperature range for an extended period of time, were the result of precipitation of some substance other than nitrides at the slip planes. Pending the adoption of a recognised term they were described as "ageing" needles.

I have only once encountered such needles. When examining three locomotive boiler crown stays which had cracked after four years' service I found that the wrought iron—said to be

Yorkshire—from which they were made contained some steel, and many of the ferrite grains contained needles which were described as ageing needles for the following reasons. First, heat-treating the specimen at 300° C. should colour nitride needles and areas containing them red; these needles were not so coloured. Secondly, nitride needles are etched out by alkaline sodium picrate; these were not. Thirdly, at a high magnification, nitride needles are seen to be double or elliptical, ageing needles are single, like pencils; these needles were single. Fourthly, when the specimen was annealed at 400° C. and cooled in air the needles disappeared; if they had been nitride needles, they would have remained.

AUTHOR'S REPLY.

The AUTHOR replied: I was very interested to receive Mr. Dinsdale's observations regarding needles sometimes observed in wrought iron and mild steel. Although I have not stated categorically that the needles observed were iron nitride I do not consider that Mr. Dinsdale's observations prove that similar needles observed by him were not a nitride. Mr. Dinsdale states that at high magnification "nitride needles are seen to be double or elliptical," whilst "ageing needles are single, like pencils." Although the majority of the needles which I have observed appear as single dark etching lines, I have frequently observed needles of appreciable breadth in juxtaposition with the other type (*see* Fig. 2). Because of the small breadth of the needles it is difficult to observe precisely colour effects produced by different methods of etching. Further, Mr. Dinsdale states that nitride needles would remain after annealing at 400° C. Surely this would only occur if the material were super-saturated with respect to the particular nitride at this temperature.

FOURTH REPORT OF THE OXYGEN SUB-COMMITTEE

OF THE COMMITTEE ON THE HETEROGENEITY OF STEEL INGOTS.¹

(Section II., Part B (b): Figs. 2 and 3 = Plates XVI. and XVII.)
 (Section III. (a): Figs. 7 to 10 = Plate XVIII.)
 (Section III. (c): Figs. 11 to 15 = Plate XIX.)
 (Section III. (f): Figs. 16 to 18 = Plate XX.)
 (Section IV. (a): Figs. 24 and 25 = Plate XXI.)
 (Section IV. (b): Fig. 26 = Plate XXII.)

Paper No. 22/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Oxygen Sub-Committee).

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(c) <i>The Aluminium Reduction Method.</i> By N. Gray, M.Met., and M. C. Sanders	242 P
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¹ A Joint Committee of The Iron and Steel Institute and The British Iron and Steel Federation, reporting to the Iron and Steel Industrial Research Council.

- (b2) *The Vacuum-Heating Apparatus at the Central Research Department, The United Steel Companies, Ltd., Stocksbridge.* By W. W. Stevenson, A.I.C., and G. E. Speight, B.Sc., A.I.C. 290 P
- (b3) *Apparatus Used at I.C.I. (Alkali), Ltd., for the Determination of Hydrogen by the Vacuum-Heating Method.* By E. W. Colbeck, M.A., and S. W. Craven, A.M.C.T. 298 P

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- (c) *The Examination of Several Rimming Steels by the Alcoholic Iodine Method and the Identification of Constituents of the Residue by X-Ray Methods.* By T. E. Rooney, A.M.S.T., F.I.C., and F. W. Jones, Ph.D. 340 P
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- (g) *Oxide Inclusions in British Pig Irons.* By J. G. Pearce, M.Sc., F.Inst.P., M.I.Mech.E. 379 P
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- (a) *The Determination of Oxygen in Liquid Steel.* By T. Swinden, D.Met., and W. W. Stevenson, A.I.C. 397 P
- (b) *The Determination of Hydrogen in Liquid Steel.* By W. H. Hatfield, D.Met., F.R.S., and W. C. Newell, Ph.D., D.I.C., A.R.C.S., A.I.C. 407 P

SECTION V.—GENERAL SUMMARY 417 P

Section I.—Introduction.

THE Third Report of the Oxygen Sub-Committee appeared as Paper No. 5/1941 of the Committee on the Heterogeneity of Steel Ingots.¹

Since the publication of the Third Report the constitution of the Sub-Committee has been modified, the present personnel being as follows :

Dr. T. Swinden (<i>Chairman</i>)	The United Steel Companies, Ltd.
Professor J. H. Andrew	The University, Sheffield.
Mr. E. W. Colbeck	I.C.I. (Alkali), Ltd., Northwich.
Mr. S. W. Craven	I.C.I. (Alkali), Ltd., Northwich.
Dr. C. H. Desch, F.R.S.	The Iron and Steel Industrial Research Council.
Dr. H. A. Dickie	Messrs. Stewarts and Lloyds, Ltd.
Mr. C. S. Graham	Messrs. John Lysaght, Ltd.
Mr. N. Gray	Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd.
Dr. A. H. Jay	The United Steel Companies, Ltd.
Dr. W. R. Maddocks	The University, Sheffield.
Dr. W. C. Newell	The Brown-Firth Research Laboratories.
Mr. J. G. Pearce	The British Cast Iron Research Association.
Dr. A. G. Quarrell	The University, Sheffield.
Mr. T. E. Rooney	The National Physical Laboratory.
Mr. H. A. Sloman	The National Physical Laboratory.
Mr. W. W. Stevenson	The United Steel Companies, Ltd.
Dr. C. Sykes, F.R.S.	The National Physical Laboratory.
Mr. W. Westwood	The British Cast Iron Research Association.
Mr. A. E. Chattin (<i>Secretary</i>)	The Iron and Steel Institute.

Mr. E. Taylor-Austin, of the British Cast Iron Research Association, resigned from the Sub-Committee in the summer of 1941 on leaving the Association and taking up a position in industry; Mr. W. Westwood, of the British Cast Iron Research Association, subsequently joined the Sub-Committee and Chemists' Panel in November, 1941. In view of a long-standing interest in the theory and practice of methods for the separation of non-metallic inclusions, Mr. C. S. Graham, of Messrs. John Lysaght, Ltd., accepted an invitation to join the Sub-Committee in November, 1941. As a result of the widening of the Sub-Committee's activities to the determination of other gases (hydrogen and nitrogen), the co-operation of Dr. A. G. Quarrell, of Sheffield University, was secured in July, 1942. It is hoped that the present Sub-Committee, which is well balanced as regards industry and purely research institutions, will continue to function unaltered for a considerable time and thereby ensure the continuity of the researches.

The Sub-Committee have continued to work well together with a keenness which is to be highly commended. A great deal of vigorous discussion has taken place in both the Sub-Committee and the

¹ *Journal of The Iron and Steel Institute*, 1941, No. I., pp. 295 P-387 P.

Chemists' Panel of the Sub-Committee. The latter body comprises those Members of the Sub-Committee who are directly concerned in the determination of the gases, oxygen, hydrogen and nitrogen, in steel, together with the following co-opted chemists :

Mr. M. C. Sanders	.	.	Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd.
Mr. C. W. Short	.	.	Messrs. John Lysaght, Ltd.
Mr. G. E. Speight	.	.	The United Steel Companies, Ltd.
Mr. T. H. Williams	.	.	Messrs. Stewarts and Lloyds, Ltd.

The fact that certain opinions expressed in the individual contributions are not necessarily held unanimously by the Members testifies to the keenness of the Sub-Committee's deliberations and augurs well for the future of their work.

The further continuance of the war has, of necessity, interfered with the smooth and regular prosecution of the various researches, and, in consequence, some aspects of the work outlined in previous Reports have not yet reached an appreciable state of finality. However, several additional problems have been investigated. Considerable attention has been devoted to the determination of gaseous elements other than oxygen, *i.e.*, hydrogen and nitrogen, as they occur in solid materials. The fundamental aspects of the residue methods and their application to a series of alloy steels have received further examination, and the determination of the gas content of liquid steel, in contradistinction to solid finished products, has been investigated and will continue to be a problem of high priority. The vacuum fusion method continues to be applied to specialised problems such as the surface film on metals.

In view of the more or less stabilised nature of the methods of examination and their extension to deal with other gases, it has been thought desirable to modify somewhat the scheme of the Sub-Committee's Reports. Section II., which is sub-divided into Parts under the main headings of Oxygen, Hydrogen and Nitrogen, deals with improvements and modifications introduced into the methods of determination of each of these elements. In each Part concise data and summaries are presented of the present state of knowledge of the methods adopted for the determination of these gases in solid steel. Section III. deals with the application of these methods to several specialised problems, *viz.*, surface films on metals, rimming steels, ferro-alloys, acid and basic slags and to a series of alloy steels, including high-silicon iron. Whilst certain of these contributions have been individual efforts, much work in others has been of a collaborative character, and the results of the Sub-Committee's co-operative examination are seen in the Section on the alloy steels (Section III. (*h*)), which is a continuation of an alloy-steel series examined in a previous Report.¹ Section IV. describes the methods

¹ Second Report of the Oxygen Sub-Committee, *Iron and Steel Institute*, 1939, *Special Report No. 25*, p. 216.

developed for the sampling of liquid steel and the determination of its gas content, whilst Section V. presents a summary of the conclusions of these individual contributions and deductions therefrom.

It is hoped that the Report will be of service to all who are interested in the subject of the gases (oxygen, hydrogen and nitrogen) in steel, and that free and frank discussion of its contents will materialise. It is only thereby that the attention of the Sub-Committee will be directed to such points as may appear to have been overlooked and the logical development of the problems assured.

Section II.—Methods of Analysis.

PART A.—DETERMINATION OF OXYGEN.

(a) *THE VACUUM FUSION METHOD*.¹

By H. A. SLOMAN, M.A. (THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON).

(Under the direction of C. Sykes, D.Sc., F.R.S.)

SYNOPSIS.

The applicability of the vacuum fusion method to the determination of the oxygen, hydrogen and nitrogen in a series of alloy steels and ferro-alloys used in steelmaking has been examined, and the sources of errors which may arise in certain cases are discussed together with recommendations for their avoidance.

The equipments in use at the various co-operating laboratories for determining oxygen by the vacuum fusion method have been fully described in previous Reports and no modifications in the equipments or alterations in technique have since been introduced. Since the publication of the last Report² considerable opportunity has been provided for a more extensive examination of the method as applied to alloy steels and to other ferrous materials such, for example, as the ferro-alloys used in steelmaking. In addition, experiments have been carried out at the National Physical Laboratory, using, as analytical samples, both powders and millings, which have necessitated the development of a simple capsule type of container of suitably low gas content. The results which have been obtained are set out in Section III. of the present Report (Examination of Materials) and it is not proposed to consider them in detail here. In the course of the work at the National Physical Labora-

¹ Received December 1, 1942.

² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 295 p.

tory, however, certain points of interest have arisen. These are chiefly in the nature of precautions which have been found necessary when dealing with certain types of material, and for the guidance of those interested in the method they are discussed below.

It is well known that one of the most serious sources of error in the vacuum fusion method is due to the volatilisation of certain metallic constituents of steel at the temperature of the experiment. This volatilisation results in the deposition on the cooler parts of the reaction vessel of highly reactive metallic films, which, if present in sufficient quantity, adsorb appreciable quantities of any gas subsequently evolved from the specimen. The recent examination of a range of alloy steels and ferro-alloys has confirmed that manganese is the most volatile of all the metals commonly present in ferrous materials. Molybdenum, copper, nickel and aluminium all tend to produce films, but to a considerably less extent. For the economical operation of the method, as many specimens as possible should be analysed at each assembly of the apparatus, but once serious film formation has commenced all later results will be too low and the apparatus must be dismantled and cleaned. It is obvious, therefore, that, wherever possible, the order in which specimens are introduced should be controlled so that those which do not lead to rapid film formation are analysed before those that contain appreciable quantities of volatile metals.

In order to examine the magnitude of the errors that can be caused by the adsorption of gas by condensed films a series of experiments was carried out using a high- (13%) manganese steel. In the first experiment, several standard specimens of this steel weighing about 20 g. each were introduced consecutively into an otherwise empty crucible, the temperature of which was held at 1560° C. This experiment was repeated several times, and on each occasion the first specimen gave an oxygen value of 0.0015–0.0020%; the second gave 0.0006–0.0010% and subsequent ones a trace to 0.0004%. A similar set of experiments was then carried out, but with this difference. The crucible, instead of being empty before the introduction of the first manganese-steel specimen, contained about 80 g. of degassed N.P.L. iron (mark 2), from which no film was formed. The results obtained in these experiments were for the first specimen 0.0017–0.0020%; for the second 0.0010–0.0015% and for subsequent ones 0.0001–0.0004%. The difference between the two sets of experiments lies in the somewhat higher figures for oxygen obtained for the second specimen in the second set. This suggests that by dilution the rate of film formation can be slowed down to some extent, but not sufficiently, under the particular conditions existing in the apparatus at the National Physical Laboratory, to make the results for more than one specimen reliable.

Experiments were then conducted in which the introduction of one manganese-steel specimen into an empty crucible was followed by specimens of a simple mild steel of known oxygen content. In

all cases the results for the carbon steel were low and outside the range of experimental error.

Attention was then directed to ascertaining whether or not the value of about 0.002% given above for the first specimen of the 13% manganese steel was itself correct. For this purpose it became necessary to know approximately how much film could be present without leading to appreciable error and also what proportion of the oxygen content of the steel was likely to be evolved and collected before that point was reached. Accordingly, a 1% manganese steel, from which the volatilisation of manganese is comparatively slow, was employed. It was found that a standard specimen of this steel could be followed by one specimen of a plain carbon steel of known oxygen content without error, and by inspection the growth of the film on the inner wall of the silica furnace tube could be watched. It was assumed that, since reliable results could be obtained on the carbon steel specimen, the film at the time of its introduction was harmless, and the general appearance of the wall of the tube at this stage was noted. Returning, now, to an investigation of the 13% manganese steel, the length of time which elapsed after the introduction of a specimen of this steel before the furnace tube wall presented a similar appearance was noted, together with the amount of gas already collected. It was found that some time before this stage was reached the rate of gas evolution had dropped practically to zero, thus suggesting that the specimen was already completely degassed and that the value of 0.002% of oxygen is very close to the true oxygen content of the steel. It may be noted that when examining this steel, the crucible temperature was deliberately kept rather low (1560° C.), but in view of the fact that in this type of steel all the oxygen is likely to be present as iron and manganese oxides, no errors due to non-reduction of stable oxides such as alumina will have been introduced.

A curious and unexpected case of film formation was first mentioned by Thanheiser and Paulus,¹ who found that, in the presence of a certain proportion of tungsten, iron itself volatilises very rapidly. They noted this effect when determining the gas content of ferro-tungsten alloys, and concluded that the vaporisable pure iron is derived from a double carbide, $\text{Fe}_3\text{W}_3\text{C}$, which by taking up further carbon is converted into W_2C and free iron. The rate of film formation from alloys containing about 80% of tungsten and 20% of iron (normal ferro-tungsten) is comparable with that from a high-manganese steel, except that in the former case the film is composed of practically pure iron. With melts which contain over 30% of iron the difficulty disappears. These conclusions have been confirmed at the National Physical Laboratory, but no other similar cases have been found in the numerous ferro-alloys examined. In general, however, it is recommended that determinations of the

¹ *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1940, vol. 22, No. 14, pp. 217-228.

gas content of ferro-alloys by the vacuum fusion method should be carried out in a bath of degassed iron or plain carbon steel, thus ensuring that the melt is iron-rich.

One exception to this general recommendation was found in the cases of silicon-iron alloys and ferro-silicons. On the first occasion when the gas content of a ferro-silicon was being determined, the specimen was introduced into a crucible already containing degassed iron. On dismantling, the crucible was found to contain, not the normal clean "button" of solid metal, but a mass which may be described as a solidified froth, which had sputtered all over the inner wall of the crucible. This froth consisted of very fine carbon and small globules of metal. Investigation of the iron-silicon-carbon system showed that the amount of carbon which dissolves in the liquid alloy decreases rapidly with increasing silicon content. When, therefore, in the experiment referred to above, a silicon-rich specimen was introduced into a crucible containing a quantity of liquid iron saturated with carbon, the immediate effect was to throw out a large amount of fine carbon, which converted the melt into a semi-pasty mass. At the same time a considerable quantity of gas was released from the ferro-silicon, and, being unable to get away freely, produced the "frothing" noted above. Subsequently, therefore, silicon-rich materials were always introduced into an empty crucible or one which already contained similar alloys. Under these conditions the melt never becomes supersaturated with carbon with respect to silicon and the evolution of gas proceeds smoothly.

As a result of the work which has been carried out since the last Report, it has been confirmed that, provided that suitable precautions are taken where necessary, the method gives accurate results for oxygen, hydrogen and nitrogen on all classes of ferrous materials. As regards oxygen, alumina is the only oxide which is sufficiently stable to present difficulties, and the examination of alloy steels containing aluminium has shown that even this oxide is quite rapidly reduced at about 1600°C . In no case has the evolution of hydrogen been found to be either incomplete or sluggish, even at temperatures as low as 1550°C . One or two nitrides which are not completely reduced at 1550°C . have been noted. They occur in steels containing chromium and titanium, but no difficulty is experienced if the reaction is allowed to proceed at 1600°C . or over.

The work described above was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research for the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

(b) *THE FRACTIONAL VACUUM FUSION METHOD FOR THE SEPARATION OF OXIDES AND GASES IN STEEL.*¹BY T. SWINDEN, D.MET., W. W. STEVENSON, A.I.C., AND
G. E. SPEIGHT, B.Sc., A.I.C.

Since the publication of the Third Report of the Oxygen Sub-Committee,² the fractional vacuum fusion method has continued to be used with success on several types of ferrous materials, including ferro-alloys and alloy steels. Results on steel samples have shown the same degree of accuracy as the selection of results published in the Third Report. Certain of the alloy steel series have been examined by this method, and the results, given in Section III.(h), indicate clearly the mode of occurrence of the oxygen-bearing inclusions.

An interesting application of the fractional procedure has been in the examination of the weld-metal deposits shown in Table I., in which it can be seen very readily that the fractional method furnishes far more information regarding the features of each particular weld deposit than does the direct total method.

The results recorded in Table I. are intended to be illustrative only of the applicability of the fractional vacuum fusion method from the analytical angle and must not be regarded as of metallurgical significance.

No essential modification of procedure has been introduced and the process is carried out as described in the Sub-Committee's Second Report.³ One of the main difficulties of the method lies in the separation of iron and manganous oxides, which, even with pure and separate oxides, is incomplete, owing to the small temperature interval between the melting point of the iron-carbon-tin alloy and the temperature at which manganese oxide is readily reduced. Attempts have been made by the use of an additional alloying metal to increase this interval by reducing the melting point and consequently the reduction temperature of the iron oxide, with the object of obtaining sharper separation of iron and manganese oxides. Additions of copper and silver have been made, with but only slight reduction of the melting point, and increased practical difficulties, such as an increased "blank," volatility of the alloy metal and reduced carbon solubility, have rendered such modifications of doubtful value.

The position remains that no other indication of the validity of the fractional method other than comparison with known residue extraction methods is as yet available. As indicated by early work, it is known that with inclusions of simple type, *e.g.*, single oxides,

¹ A communication from the Central Research Department, The United Steel Companies, Ltd. (Stocksbridge, Sheffield), received March 19, 1943.

² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 295 p.

³ Eighth Report on the Heterogeneity of Steel Ingots, p. 63, *Iron and Steel Institute*, 1939, *Special Report No. 25*.

TABLE I.—*Determination of Oxygen in Weld-Metal Deposits by the Fractional Vacuum Fusion Method.*

Sample No.	Type of Welding Rod Used.	Weld-Deposit Analysis.			
		C. %.	Mn. %.	Si. %.	Mo. %.
1	Covered class A electrode with cotton string.	0.08	0.65	0.04	...
2	Covered class A electrode with asbestos coating.	0.06	0.42	0.095	0.32
3	Covered class A electrode with no string.	0.08	0.43	0.165	0.36
4	Covered class A electrode with asbestos string.	0.04	0.48	0.105	...
5	Covered class B electrode with asbestos string. Low-manganese type.	0.08	Nil	Trace	...
6	} Covered class A electrode { with cotton string.	0.06	0.33	0.085	...
7		0.09	0.52	0.10	...
8	Covered class A electrode with cotton string.	0.07	0.33	0.03	...

Sample and Type of Weld.	Oxygen.		Hydrogen.		Nitrogen. %.
	Oxygen. %.	Oxide. %.	Ml. per 100 g.	%.	
Weld Metal No. 1 :					
FeO fraction .	0.033	0.149	12.0	0.00108	0.0025
MnO " .	0.008 ₅	0.039	0.0020
SiO ₂ " .	0.005 ₅	0.010 ₅	0.0034
Al ₂ O ₃ " .	0.022	0.047	0.0128
Total .	0.069	0.245 ₅	12.0	0.00108	0.021
Weld Metal No. 2 :					
FeO fraction .	0.016	0.073	11.5	0.00104	0.0048
MnO " .	0.020 ₅	0.091	0.0040
SiO ₂ " .	0.016	0.030	0.0046
Al ₂ O ₃ " .	0.023	0.048	0.0056
Total .	0.075	0.241	11.5	0.00104	0.019
Weld Metal No. 3 :					
FeO fraction .	0.005 ₅	0.025	14.0	0.00126	0.0013
MnO " .	0.022	0.098	0.0038
SiO ₂ " .	0.023	0.044	0.0046
Al ₂ O ₃ " .	0.021	0.044	0.0094
Total .	0.071 ₅	0.210	14.0	0.00126	0.019
Weld Metal No. 4 :					
FeO fraction .	0.004 ₅	0.019	8.4	0.00075	0.0043
MnO " .	0.052	0.229	0.0095
SiO ₂ " .	0.023	0.043 ₅	0.0105
Al ₂ O ₃ " .	0.012	0.025	0.0056
Total .	0.091 ₅	0.317 ₅	8.4	0.00075	0.030

TABLE I.—(continued).

Sample and Type of Weld.	Oxygen.		Hydrogen.		Nitrogen. %.
	Oxygen, %.	Oxide, %.	Ml. per 100 g.	%.	
Weld Metal No. 5 :					
FeO fraction .	0.212	0.951	8.8	0.00079	0.0056
MnO " .	0.011	0.049	0.0056
SiO ₂ " .	0.005	0.009 ₅	0.0081
Al ₂ O ₃ " .	0.004	0.008	0.0043
Total . . .	0.232	1.017 ₅	8.8	0.00079	0.024
Weld Metal No. 6 :					
FeO fraction .	0.015	0.068	10.0	0.00090	0.0117
MnO " .	0.029	0.128	0.0060
SiO ₂ " .	0.026	0.048	0.0065
Al ₂ O ₃ " .	0.019	0.041	0.0070
Total . . .	0.089	0.284	10.0	0.00090	0.031
Weld Metal No. 7 :					
FeO fraction .	0.014	0.063	12.0	0.00108	0.0130
MnO " .	0.020	0.088	0.0049
SiO ₂ " .	0.021	0.039	0.0075
Al ₂ O ₃ " .	0.025	0.053	0.0069
Total . . .	0.080	0.243	12.0	0.00108	0.032
Weld Metal No. 8 :					
FeO fraction .	0.040	0.181	13.6	0.00122	0.0043
MnO " .	0.043	0.189	0.0045
SiO ₂ " .	0.029	0.055	0.0072
Al ₂ O ₃ " .	0.036	0.075	0.0040
Total . . .	0.148	0.501	13.6	0.00122	0.020

separation is reasonably accurate, although this may not hold for more complex compounds. The authors therefore much appreciate the kindness of Professor Hay, of Glasgow, in having recently supplied specimens of definite steelmaking compounds such as fayalite, rhodonite, tephroite, &c., for the fundamental investigation of the fractional procedure. The technique adopted is the fractional reduction of a synthetic sample comprising known mixtures of the compounds and oxygen-free iron, Mark 2, supplied by the National Physical Laboratory; early experiments have indicated the practical difficulties of this method, arising from the "clotting" effect of the compound during fusion similar to that observed in the examination of the acid and basic slags (*see* Section III.(e)).

Further experience of the fractional method has confirmed previous findings regarding the significance of fractional results on

normal killed steels. In comparison with residue methods there is a tendency for :

- (a) The iron-oxide fraction to be lower,
- (b) the manganese-oxide fraction to be higher, and
- (c) silica and alumina results to be lower.

The authors regret that, owing to pressure of other work due to existing conditions and failure to obtain satisfactory synthetic materials until comparatively recently, it has not been possible to carry out research on the lines suggested by Dr. McCance in his contribution to the discussion of the Sub-Committee's Third Report. However, it is definitely planned to determine rates of gas evolution at specific temperatures on the previously mentioned oxides and silicates supplied by Professor Hay. This work has, in fact, commenced and will be pursued as opportunity permits.

(c) *THE ALUMINIUM REDUCTION METHOD.*¹

By N. GRAY, M.MET., and M. C. SANDERS (MESSRS. GUEST KEEN BALDWIN'S IRON AND STEEL CO., LTD., PORT TALBOT).

Reduction in a Hydrogen Atmosphere.

Since the publication of the Third Report² there has been no alteration in the apparatus or the method of manipulation up to the production of the iron-aluminium alloy.

Analytical Procedure.

The analytical procedure has remained unchanged for work on alloy steels and slags, except in the case of tungsten-bearing steel (No. 10 in the series of thirteen alloy steels, *see* Section III.(h)) and 4% silicon transformer iron (*see* Section III.(f)). With regard to tungsten steel, there is a precipitation of tungstic acid, which is removed from the alumina residue after the first wash with acid and hot water by treatment with ammonium hydroxide and finally hot water before ignition.

Reduction in Vacuo.

It is suggested that in view of the fact that in this modification the work is not being carried out in a true vacuum, the description should be altered to "under reduced pressure."

At the Central Research Department of The United Steel Companies, Ltd., two modifications have been introduced :

- (1) The furnace tube and rubber bung have been replaced by a silica tube and ground joint, the ground joint being con-

¹ Received December 16, 1942.

² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 321 p.

nected to a Pyrex adaptor and stopcock. This is to minimise the possible air leak to the evacuated tube when using the older apparatus.

(2) A modified graphite boat, incorporating a detachable lid, is now used. The purpose is to reduce possible error due to small pieces of silica being flaked from the tube and falling into the aluminium-alloy metal, thereby reacting to form alumina.

(d) *THE CHLORINE METHOD.*¹

By E. W. COLBECK, M.A., AND S. W. CRAVEN, A.M.C.T.
(NORTHWICH).

SYNOPSIS.

Experiments on the effect of increased chlorination temperature on the recovery of oxide inclusions from fully killed steels are described, and the possible conclusions to be drawn from the results are discussed.

The application of the chlorine method to some of the steels from the Oxygen Sub-Committee's alloy-steel series is referred to, and the results obtained by two laboratories using the method are reviewed.

Introduction.

In the Third Report of the Oxygen Sub-Committee, Section IV., Part B,² the applicability and utility of the chlorine method for the determination of oxide inclusions in steel were discussed. Up to that time the work on the chlorine method had been largely confined to the examination of a number of plain carbon steels and of a series of steels containing amounts of alloying elements of the order of 0.5%. A chlorination temperature of 350° C. was employed for all these steels except that containing 0.5% of chromium, and under these conditions the agreement for total oxygen between the chlorine and the vacuum fusion methods was satisfactory. A rimming steel, as distinct from the fully killed steels, gave less satisfactory results.

When a more detailed examination of the behaviour of alloying elements was contemplated, the necessity for more precise knowledge as to the effect of increased chlorination temperature on the various oxide constituents of a non-metallic residue was at once obvious. It was known that particular difficulties would be encountered with steels containing significant amounts of chromium. In the first place, during the chlorination of a chromium-bearing steel, the chromium is converted to chromic chloride, which is neither volatile at 350° C. nor soluble in water. Secondly, increasing chromium content causes a big increase in the resistance of the steel to attack by chlorine. The first difficulty might be overcome in one of two

¹ Received December 1, 1942.

² *Journal of The Iron and Steel Institute*, 1941, No. I., pp. 339 P-344 P.

ways: (a) By using a suitable reducing agent to convert any chromic chloride formed during chlorination at 350°C . to the water-soluble chromous chloride, or (b) by increasing the chlorination temperature to a point at which the chromic chloride is volatile. As, however, chlorination temperatures above 350°C . would have to be used for steels with appreciable chromium contents, it was felt that attention should first be given to the effect on the oxide inclusions of increases in reaction temperature up to 700°C . For this purpose a sample of basic open-hearth boiler plate, previously examined by Swinden, Stevenson and Speight, was chosen, as the alcoholic iodine and fractional vacuum fusion results obtained on it suggested that MnO , the oxide likely to be most sensitive to increased attack with rising chlorination temperature, was present in amounts rather greater than those normally found in good-quality commercial steels.

The Method and the Apparatus Used.

The chlorination procedure used was identical with that described in the Third Report of the Oxygen Sub-Committee, Section IV., Part A. For chlorination temperatures above about 550°C ., the Pyrex glass reaction tube was unsuitable, and so a second apparatus was constructed with a transparent silica reaction tube and thermocouple carrier. Experiments carried out in this apparatus, using the standard steel referred to in the Section of the Third Report of the Oxygen Sub-Committee mentioned above, showed that results for oxide inclusions similar to those obtained in the glass apparatus were secured.

Increased Chlorination-Temperature Experiments.

Experiments on the effect of increased chlorination temperature were carried out, using a sample of basic open-hearth boiler plate provided by The United Steel Companies, Ltd., Central Research Department. Its chemical analysis was as follows:

Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.
0.14%	0.63%	0.014%	0.046%	0.035%

Solid test-pieces were chlorinated at 350° , 450° , 500° , 550° and 700°C . In another experiment the usual chlorination procedure at 350°C . was followed and after the reaction was completed the residue was heated for a further three-quarters of an hour at 600°C ., the stream of chlorine being maintained throughout this period. All chlorinations except that at 350°C . were carried out in the transparent silica apparatus. The results obtained are given in Table II., together with figures obtained by the Central Research Department using the vacuum fusion and alcoholic iodine methods.

Since the work on the effect of increased chlorination temperature has been confined to the examination of one sample of steel, it is obvious that no definite conclusions can be drawn from the

TABLE II.—*Experiments on the Influence of Increased Chlorination Temperature, Using a Sample of Basic Open-Hearth Boiler Plate.*

Details of Method Used.	Total Ignited Residue. %.	SiO ₂ .		FeO.		MnO.		Al ₂ O ₃ .		Cr ₂ O ₃ . %.	P ₂ O ₅ . %.	Total Oxygen. %.
		%.	O ₂ . %.	%.	O ₂ . %.	%.	O ₂ . %.	%.	O ₂ . %.			
Direct vacuum fusion *	.	0.022	0.0118	0.007 ₆	0.0017	0.033	0.0075	0.013	0.0062	0.027
Fractional vacuum fusion °	.	0.026	0.0138	0.011	0.0024	0.033	0.0074	0.014 ₅	0.0068	0.027
Alcoholic iodine *	.	0.023 ₈	0.0125	0.009	0.0020	0.032	0.0072	0.013 ₈	0.0064	0.010 ₅	0.010 ₅	0.030 ₆
Chlorination at:	.									0.010 ₅	0.010 ₅	0.028
350° C.	.	0.022	0.0117	0.010 ₅	0.0023	0.033	0.0074	0.013	0.0062	0.075	0.001	0.027 ₈
450° C.	.	0.023	0.0124	0.007 ₈	0.0017	0.035	0.0080	0.012 ₈	0.0059	0.014	0.001 ₅	0.028
500° C.	.	0.022	0.0118	0.007 ₈	0.0017	0.034	0.0077	0.012 ₈	0.0059	N.D.	0.001	0.027
550° C.	.	0.022	0.0117	0.005 ₈	0.0011	0.031	0.0070	0.012 ₈	0.0058	N.D.	0.001	0.025 ₆
700° C.	.	0.049	0.0105	0.004 ₅	0.0010	0.012	0.0028	0.011 ₅	0.0054	N.D.	0.001	0.019 ₆
350° C., followed by heating at 600° C. for ½ hr. in chlorine stream	.	0.074	0.021	0.004 ₅	0.0011	0.030 ₅	0.0069	0.013	0.0062	N.D.	0.001	0.024 ₅

* Figures obtained by The United Steel Companies, Ltd., Central Research Department.

N.D. = Not detected.

results shown in Table II. The figures do, however, give a general indication of the behaviour of the various oxides when the basic oxides are combined with silica and alumina and are not present simply as FeO or MnO. It will be seen that both the SiO_2 and Al_2O_3 fractions remain substantially unaffected by an increase in temperature up to at least 550°C . The small decrease in the recovery of the two oxides at 700°C . may be significant of the commencement of attack. At 450°C . the recovery of FeO is slightly less than at 350°C ., while at 550°C . the amount of this oxide remaining in the residue represents only about 50% of that retained at 350°C . The amounts of MnO found in the residues appear to be fairly constant up to 500°C ., but at 700°C . the rate of attack is rapid.

These broad conclusions drawn from the results in Table II. are consistent with the findings of Wasmuht,¹ who approached the problem from a rather different angle. He examined the behaviour of a number of synthetic oxides and naturally occurring silicates at different temperatures in a stream of chlorine, and showed that attack on SiO_2 and Al_2O_3 , even in the presence of carbon, did not begin until 700°C . It was also shown that FeO and MnO combined with SiO_2 in the minerals grünerite ($\text{FeO}.\text{SiO}_2$), fayalite ($2\text{FeO}.\text{SiO}_2$), rhodonite ($\text{MnO}.\text{SiO}_2$) and tephroite ($2\text{MnO}.\text{SiO}_2$) were much more resistant to attack by chlorine than they were in the free state, and that an increase in the base-to-acid ratio in the minerals also led to more rapid attack on the basic oxides.

The figures in Table II. also throw some light on the behaviour of chromic chloride formed during chlorination. At 350°C . chromic chloride is, apparently, non-volatile in the chlorine stream, and as it is insoluble in water it is retained in the residue and subsequently ignited to Cr_2O_3 . At 450°C . some volatilisation occurs, but the rate is slow and some chloride still remains in the residue. At temperatures of 500°C . and over, however, the volatilisation of the small amount of chromic chloride formed with the particular steel under examination is complete, and no Cr_2O_3 was found in the residues. Other work by the authors has suggested, however, that the rate of volatilisation of chromic chloride is slow at 500°C . and that considerable amounts of the water-insoluble salt are left behind in residues obtained from steels containing appreciable percentages of chromium after chlorination at that temperature.

The excellent agreement existing for the various oxide fractions obtained by the fractional vacuum fusion, the alcoholic iodine and the chlorine methods on this sample of boiler plate is worthy of mention here.

The Examination of some of the Steels in the Sub-Committee's Alloy-Steel Series.

When the Oxygen Sub-Committee chose, for co-operative examination, a series of thirteen alloy steels (for details of com-

¹ *Zeitschrift für angewandte Chemie*, 1930, vol. 43, pp. 98-101, 125-129.

position, method of manufacture, gas analyses, &c., *see* Section III.(h)), representing a wide range of commercial alloys, it was hoped that a careful study of each would discover the modifications to be made in the chlorine method as required by the presence of different alloying elements in varying proportions. Unhappily it has been possible to complete determinations by the chlorine method on a limited number of these steels only, so that this paper must be regarded as an interim statement, covering but a small portion of the whole field.

The steels numbered 1, 2, 3, 7 and 11 have been examined by the authors, using chlorination temperatures of 350° and 500° C. in each case, the transparent-silica apparatus being employed at the higher temperature. The chlorine method at 350° C. has also been used to determine oxide inclusions in steels 1, 2, 3 and 11 by Dickie and Williams, of Messrs. Stewarts and Lloyds, Ltd. These workers have employed an apparatus and technique similar to that described by Colbeck, Craven and Murray in the Third Report of the Oxygen Sub-Committee, Section IV., Part A, except that a current of dry compressed air is not used for cooling the reaction tube after the preliminary heating. Instead, the furnace is so arranged that one side of it, together with the insulating material, can be removed, thereby effecting a comparatively rapid cooling of the reaction tube.

No difficulties in manipulation or analysis were encountered with steels Nos. 1, 2, 3 and 11. With steel No. 7 the reaction was slow at 350° C. and chlorination was not complete in 4 hr. At the end of that time it was found that each of the four metal discs used was in the form of a pellet consisting of a thin inner core of undecomposed metal, non-metallic matter and carbon, bound together with purple chromic chloride. In order to complete the analysis, the residual chromic chloride was reduced and the slips of metal were separated from the non-metallics and carbon and then dried and weighed. Their combined weight was deducted from the original weight of sample taken. At 500° C. the reaction with sample No. 7 was much more rapid and the separation of chromic chloride, though not quite complete, was much better than at 350° C.

The results obtained show good agreement between the two laboratories operating the chlorine method, and the calculated total oxygen contents are similar to those obtained by the vacuum fusion method. It would appear that the chlorine method is not subject to interference from aluminium carbide and/or nitride in steels Nos. 1, 2 and 3, as is the case with the alcoholic iodine method (but *see* Section II., Part A(e3)).

The difficulties experienced with steel No. 7 are further indications of the comparatively slow rate of volatilisation of chromic chloride in the chlorine stream, even at 500° C.

(e) *THE ALCOHOLIC IODINE METHOD.*¹

BY T. E. ROONEY, A.M.S.T., F.I.C. (THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON).

(Under the direction of C. Sykes, D.Sc., F.R.S.)

SYNOPSIS.

A critical summary is presented of the work carried out on the alcoholic iodine method.

Since the publication of the Third Report of the Oxygen Sub-Committee² no alterations have been made in the apparatus or the mode of operation of the alcoholic iodine method, but attention has been directed towards the removal of certain limitations, thus extending the applicability of the method.

In the present Report factors affecting the presence of phosphorus in the residue have been further investigated. It has already been established that the use of samples in the form of discs instead of millings and of deoxidised alcoholic iodine solution reduces the amount of contamination of the residue by phosphorus.³

In the first investigation described below (part (e1)), in which Stevenson and Speight collaborated, it was demonstrated that small amounts of water in the methanol had no effect on the amount of phosphorus retained in the residue but that the presence of water caused an increase in the percentage of iron oxide. The increase in the iron oxide appeared to be greater with the "boiling" than with the "stirring" method.

In another investigation (part (e2)) Speight demonstrated the possibility of the adsorption of phosphorus by the free carbon formed by the decomposition of iron carbide, and, what is especially satisfactory, he devised a simple method (*i.e.*, treatment with boiling ammonium tartrate solution) for the removal of much of the phosphorus contamination. Evidence in support of his conclusion is based on the relation between the percentage of carbon and phosphorus in the steel and the amount of P_2O_5 in the ignited residue. As further evidence regarding adsorption may be added the fact that several attempts to separate the carbon from the other constituents of the unignited residue have failed, possibly owing to their intimate admixture. It also appears to be impossible in the presence of much free carbon to identify the metallic constituents of the residue by X-ray methods.

In Table III. the results obtained on a number of steels with varying carbon and phosphorus contents have been collected together.

¹ Received April 15, 1943.

² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 295 F.

³ Rooney, Second Report of the Oxygen Sub-Committee, p. 156, Table XLII., *Iron and Steel Institute*, 1939, *Special Report No. 25*.

The steels were examined by the "boiling" or "stirring" methods, using discs. The results have been plotted in the form of a "contour" graph (Fig. 1) which serves to illustrate the relationship of the phosphorus retained in the residue (expressed as P_2O_5) to the percentage of carbon and phosphorus in the steel.

TABLE III.—*Variation of the Amount of P_2O_5 Retained in the Residue with the Percentage of Carbon and Phosphorus in the Steel.*

Sample.	Carbon in the Steel. %.	Phosphorus in the Steel. %.	P_2O_5 in the Ignited Residue. % of steel.	Reference.
Pure Fe + P	0.01	0.053	Trace	3rd Report, Table XVII., p. 52.
Rimming steel	0.03	0.011	0.003-0.005	" " " XVIII., p. 52.
1753	0.04	0.041	0.001-0.002	4th " Section III.(c).
52,703	0.08	0.010	0.001	" " " III.(b), Table V.
4360	0.11	0.092	0.006	" " Section II.(e2).
1	0.13	0.029	0.004	3rd " Table XX.
52,363	0.14	0.037	0.003	" " " XXIV.
Top plate	0.14	0.036	0.008	4th " Section II.(e1).
6972	0.16	0.043	0.004	" " " III.(c).
398/12	0.17	0.072	0.004	" " " " "
4	0.17	0.014	0.005	3rd " Table " XVII.
52,308	0.18	0.051	0.005-0.007	" " " " " XXIV.
5	0.22	0.020	0.006	" " " " " XXIV.
9273	0.22	0.021	0.003	4th " Section III.(c).
1	0.28	0.009	0.004	" " " " " III.(h).
2	0.28	0.010	0.003-0.005	" " " " " " "
3	0.30	0.058	0.014	" " " " " " "
2694	0.30	0.163	0.017	2nd " Table " LVII., p. 214.
1269	0.31	0.086	0.013-0.017	" " " " " LVI., p. 212.
1267	0.32	0.009	0.001	" " " " " LIV., p. 208.
1268	0.33	0.094	0.014	" " " " " LV., p. 210.
3	0.39	0.027	0.013	3rd " " " " " XX.
6	0.43	0.014	0.006	" " " " " XVII.
BA	0.57	0.022	0.004	N.P.L.
6	0.58	0.025	0.015	3rd Report, Table XX.
KS	0.60	0.025	0.004	N.P.L.
KE	0.86	0.027	0.006	" " " " " " "
4105	1.06	0.019	0.015	4th Report, Section II.(e).
4104	1.08	0.114	0.031-0.036	" " " " " " "

The paper by Speight (e2) also deals with the adsorption of iron, and the treatment for its removal is more successful than for phosphorus.

The relationship between the carbon content of the steel and the FeO fraction of the residue is indicated in Table IV. For this Table samples were chosen with the carbon varying from 0.009% to 1.08% and total oxygen (vacuum fusion) from 0.0023% to 0.010%. It will be noted that between about 0.60% and 0.70% of carbon the oxygen equivalent of the FeO tends to exceed the total oxygen value, indicating that the residue contains an excessive amount of iron. Above 0.70% of carbon the excess of iron is more pronounced (see Table IV.).

These steels also contain other oxides, data for which are contained in this and previous Reports. In the case of the higher-carbon samples, the combined effect of these oxides and the FeO gives a

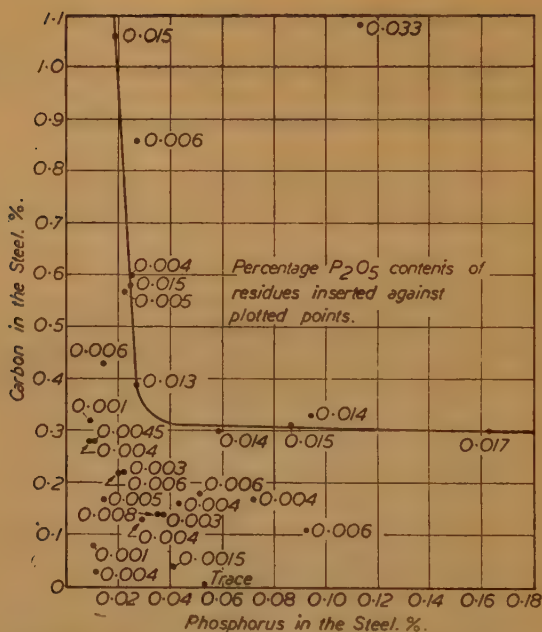


FIG. 1.—Variation of the P_2O_5 Content of the Residue with the Percentage of Carbon and Phosphorus in the Steel.

TABLE IV.—Variation of the FeO Fraction of the Residue with the Percentage of Carbon in the Steel.

Sample.	Carbon in the Steel. %.	Iron in the Residue expressed as FeO. % of steel.	Oxygen Equivalent of FeO. %.	Total Oxygen by Vacuum Fusion. %.
EH6	0.009	0.004–0.005	0.0010	0.0028
52,703	0.08	0.004	0.0009	0.004
6,972	0.16	0.0073	0.0016	0.005
398/12	0.17	0.010	0.0022	0.007
2	0.28	0.007	0.0016	0.010
3	0.30	0.008	0.0018	0.007
3A	0.39	0.008	0.0018	0.0035
BA	0.57	0.016	0.0036	0.008
5	0.58	0.011	0.0025	0.0023
KS	0.60	0.021	0.0047	0.007
R75	0.77	0.038	0.0085	0.0029
KE	0.86	0.035	0.0078	0.005
4105	1.06	0.028	0.0065	0.004
4104	1.08	0.050	0.0110	0.005

value for total oxygen appreciably in excess of the vacuum fusion figure.

The effect of the increasing carbon content on the iron content of the residue could probably be more accurately determined from a series of iron-carbon alloys.

The possibility of the adsorption of other constituents such as silica is also referred to, and in an Appendix to paper (e2) some experiments on the adsorption of aluminium are described which are dealt with later.

The last paper in this series (part (e3)) describes experiments, in which Short collaborated, on residues from three aluminium steels Nos. 1, 2 and 3 (alloy steel series, Section III.(h)). A nitrogen determination on an unignited residue from steel No. 3 indicated that about 50% of the nitride contained in the steel was not decomposed by the alcoholic iodine solution. Some experiments on a sample of aluminium carbide illustrated that this carbide is only slowly decomposed by the iodine solution. The examination of the three steels by the iodine method yielded ignited residues containing a high proportion of alumina, probably due to the retention in the residue of undecomposed aluminium compounds other than alumina.

Experiments were made with three methods of treating the unignited residue in order to remove these undecomposed compounds. The corrected results so obtained were in good agreement with the vacuum fusion value.

Reference is also made in the paper to the examination of steels No. 7 (3.5% nickel, 0.7% chromium), No. 8 (4.5% nickel, 1.25% chromium) and No. 12 (18% chromium, 8% nickel) of the alloy steel series. The results on these steels, considering their complexity, are satisfactory.

In the Appendix by Speight, referred to above, experiments are described on one low-carbon and two high-carbon steels which indicate the possibility of the adsorption of aluminium by the free carbon formed by the decomposition of iron carbide during the reaction in the iodine solution. The contamination by the aluminium can be removed by the application of the methods referred to above or by treatment with 10% ammonium tartrate solution.

The adsorption of aluminium is more probable with the "boiling" than with the "stirring" method, because with the former method the free carbon is retained in the form of compact discs similar in size and shape to the original steel discs, while with the latter the discs are mostly broken up and the free carbon is in the form of a fine suspension. It may be mentioned that during the ignition of residues from the stirring method only slight traces of iodine could be detected.

As a result of the work described in the three papers here summarised, it can be stated that the range and usefulness of the alcoholic iodine method have been extended and some of the limitations listed in the previous Report have been removed.

In Section III.(c) the results are given of an examination of several rimming steels by the alcoholic iodine method. Successful results were obtained by the standard iodine-method procedure on three steels containing over 0.15% of carbon.

A basic Bessemer steel of low carbon (0.04%) and high oxygen (0.027%) content and containing only traces of silicon and aluminium gave low results for total oxygen by both the standard and a modified procedure. A successful result had previously been obtained on a steel of very similar composition by the modified procedure.¹ X-ray examination showed that residues separated by the modified procedure tended to retain undecomposed manganese sulphide. Heat treatment of the steel, while producing a small improvement in the amount of oxide recovered, increased the tendency for the retention of manganese sulphide and sometimes of cementite. It is evident, therefore, that steels of this type (*viz.*, low-carbon high-oxygen and with traces of silicon and aluminium) may give low results for total oxygen by the iodine method even by the modified procedure.

X-ray examination failed to detect any oxide in any of the residues, except in one case, where a faint trace of manganous oxide was detected.

Subsequently a vacuum fusion determination on a residue indicated the presence of an amount of oxygen of approximately the same order as that determined by the modified iodine procedure on a heat-treated sample of the steel.

(el) *The Water Content of Methanol and its Effect on Results by the Alcoholic Iodine Method.*²

By T. E. ROONEY, A.M.S.T., F.I.C. (THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON).

(Under the direction of C. Sykes, D.Sc., F.R.S.)

SYNOPSIS.

A method of determining the water content of methanol by means of density measurements with sensitive hydrometers is described.

The effect on the water content of the distillation of the methanol over calcium is discussed.

Experiments on the effect of the water content of the methanol on results by the alcoholic iodine method are described.

The Use of Hydrometers.

The need has been felt for some method of checking and controlling the "dryness" of batches of methanol. A convenient method is

¹ Rooney, Third Report, *loc. cit.*, Section V., Part A, Table XVIII., p. 346 P.

² Received, November 27, 1942.

to determine the density, and this can be done with considerable accuracy by the use of sensitive hydrometers.

The International Critical Tables, vol. III., p. 116, gives densities at 0°, 10°, 15·56° and 20° C. based on the work of Dittmar and Fawsitt¹ and densities at 15° C. from Doiroshevskii and Rozdestvenskii's paper.² For a given density in the neighbourhood of 100% methanol, the percentage of methanol is about 0·2% lower on the basis of the Doiroshevskii and Rozdestvenskii values than on that of the Dittmar and Fawsitt values.

On the assumption that possibly final traces of water were more successfully removed in the later determinations these have been accepted for the preparation of Table V.; the values of density at 15° C. for 99% and 100% methanol of Doiroshevskii and Rozdestvenskii were reduced to density at 20° C. by means of the value 0·00092 g. per ml. per °C. for the change in density with temperature deduced from Dittmar and Fawsitt values, and the Table was obtained by linear interpolation between these two values of density at 20° C.

TABLE V.—*Density and Composition of Methanol-Water Mixtures at 20° C.*

Density at 20° C. G. per ml.	Percentage of Methanol.	Density at 20° C. G. per ml.	Percentage of Methanol.
0·791 ₁₇	100·00	0·791 ₉	99·7 ₄
0·791 ₃	99·9 ₉	0·792 ₀	99·7 ₁
0·791 ₃	99·9 ₅	0·792 ₁	99·6 ₇
0·791 ₄	99·9 ₃	0·792 ₂	99·6 ₄
0·791 ₅	99·8 ₈	0·792 ₃	99·6 ₁
0·791 ₆	99·8 ₅	0·792 ₄	99·5 ₈
0·791 ₇	99·8 ₁	0·792 ₅	99·5 ₄
0·791 ₈	99·7 ₈	0·792 ₆	99·5 ₁

Two hydrometers have been obtained, one of nominal range 0·786–0·792 g. per ml. and the other 0·792–0·798 g. per ml. The scales of the hydrometers have 60 sub-divisions in the nominal range, and thus the density equivalent of each sub-division is 0·0001 g. per ml., so that one sub-division is equivalent to 0·04% of methanol. With a little practice the sub-divisions can be divided by 5 by visual observation.

These hydrometers have been tested in the Metrology Department of the National Physical Laboratory. A correction is necessary for the scale error (this correction being derived from the N.P.L. calibration certificate) and for the difference in volume of the hydrometer at the temperature at which it is read and its volume at 20° C.

At the National Physical Laboratory the methanol is usually received in 10-gal. metal drums; is transferred to clean dry win-

¹ *Proceedings of the Royal Society of Edinburgh*, 1897, vol. 33, p. 509.

² *Journal of the Russian Physico-Chemical Society*, 1909, vol. 41, p. 1428.

chesters and the stoppers are sealed. After such transfer the density at 20° C. is usually 0.7919 ± 0.0001 g. per ml., but a recent consignment was found to be of density 0.7916_5 g. per ml. and therefore ready for immediate use without distillation.

To ensure that the methanol is dry the usual practice has been to distil over calcium two or three times. The use of the hydrometers over an extended period has indicated that there is seldom any advantage in distilling over calcium more than once if the density is in the neighbourhood of 0.7919 g. per ml. With one distillation the density can be reduced from 0.7919 to 0.7916_5 g. per ml., and a further distillation may tend to increase rather than reduce the lower value.

Alcohol recovered by filtration or decantation from the lime residues has a density at 20° C. of round about 0.7935 g. per ml., and needs up to four distillations over calcium in order to obtain a density of 0.7917 g. per ml. It is usually distilled once over calcium and used for cleaning purposes, &c.

The Effect of Water on the Composition of Residues Produced by the Alcoholic Iodine Method.

Some work has been reported by the British Cast Iron Research Association on the effect on the constituents of the iodine residue of the addition of a small amount of water to the alcoholic iodine solution.¹ The results showed a reduction in the value for silica with the addition of water, a slight increase in the ferric oxide value and a large increase in the percentage of phosphorus with an addition of 0.5% of water.

During the investigation of a pig iron containing 1.48% of phosphorus by the alcoholic iodine method Colbeck and his co-workers obtained a value of 0.012% of P_2O_5 in the residue. It was difficult to repeat this low value until a careful distillation of the alcohol had been made, indicating that air and/or traces of water in the solvent have some effect on the retention of P_2O_5 in the residue. The higher results for P_2O_5 usually found in residues from cast iron had previously been regarded as being due to the insolubility of iron phosphide in the alcoholic iodine solution.

During the examination of a mild steel containing 0.028% of phosphorus, variations of from 0.003% to 0.02% of the P_2O_5 fraction of the residue were observed. When special attention was paid to the distillation and drying of the alcohol (by repeated distillations over calcium) the low value could be repeated, and this result appeared to link up with the work described above. It was subsequently found, however, that the high phosphorus values were due to an accidental "blank," but the occurrence directed attention

¹ Second Report of the Oxygen Sub-Committee, Eighth Report on the Heterogeneity of Steel Ingots, p. 168, *The Iron and Steel Institute*, 1939, *Special Report No. 25*.

to the fact that repeated distillation of the methanol over calcium might not have the effect of removing all traces of water.

In order to confirm that the high P_2O_5 values obtained on the mild steel were due to a "blank" and not to traces of water in the methanol, two determinations were made by the alcoholic iodine method, using (1) methanol of density 0.7918 g. per ml., (2) the same methanol with the deliberate addition of 0.5% of water, the density of this mixture being 0.7936 g. per ml. The results are as follows :

	(1.)	(2.)
Density of methanol at 20° C. .	0.7918 g. per ml.	0.7936 g. per ml.
Amount of P_2O_5 in the residue :	0.0031%	0.0028%

These results indicate that the addition of water to "dry" methanol does not cause an increase in the percentage of P_2O_5 retained in the residue.

TABLE VI.—*The Effect of the Addition of Water to the Methanol on the Constituents of the Residue.*

	Steel SG1268.		Basic Open-Hearth Steel 9273/1P.	
Carbon. % . . .	0.33		0.22	
Silicon. % . . .	0.25		Trace	
Sulphur. % . . .	0.017		0.045	
Phosphorus. % . .	0.094		0.021	
Manganese. % . . .	0.67		0.60	
Titanium. % . . .	0.007		...	
Density of alcohol at 20° C.	0.7937		0.7917 ₅	
Alcohol (calc.). % .	99.18		99.80	
Total ignited residue. %	0.067		0.050	
	0.065		0.0565	
SiO ₂ . %	0.010	0.005 ₄	0.010	0.005 ₄
FeO. %	0.005 ₄	0.001	0.011	0.002 ₅
Al ₂ O ₃ . %	0.009 ₂	0.004 ₄	0.011	0.005 ₁
MnO. %	0.011	0.002 ₈	0.007	0.001 ₈
TiO ₂ . %	0.013	0.010	0.010	0.010
Cr ₂ O ₃ . %	0.0005	0.001	Trace	0.001
P ₂ O ₅ . %	0.014	0.013	0.003	0.003
Total oxygen :				
Iodine method	0.013	0.014 ₃	0.014	0.016
Vacuum fusion method	0.013		0.013	

This experiment was repeated on two other steels, *viz.*, SG1268, containing 0.094% of phosphorus, and 9273/1P, containing 0.021% of phosphorus. The results are given in Table VI.; they confirm the previous conclusion that the addition of 0.5% of water to "dry" methanol does not cause an increase in the percentage of P_2O_5 retained in iodine residues. The addition of water causes an increase in the percentage of FeO retained in the residue, and this result is in line with earlier work, but it is probable that this effect would be much more pronounced if the methanol contained dissolved oxygen in addition to the water.

Similar experiments were made at the Central Research Department of The United Steel Companies, Ltd., by the "boiling" method,¹ using the methanol as received and after two distillations over calcium. The sample used was the boiler plate reported on as "top plate" in Table IV., p. 313 P of the Third Report of the Oxygen Sub-Committee. It was made in the basic open-hearth furnace and its analysis was :

Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0.14%	0.014%	0.046%	0.035%	0.63%

TABLE VII.—*The Effect of the Use of Methanol as Received and after Distillation over Calcium.*

					Methanol Distilled twice over Calcium.	Methanol as received.
Total ignited residue.	%	.	.	.	0.114	0.131
SiO ₂ .	%	.	.	.	0.027	0.026
FeO.	%	.	.	.	0.014	0.027
MnO.	%	.	.	.	0.040	0.040
P ₂ O ₅ .	%	.	.	.	0.008	0.008
Al ₂ O ₃ .	%	.	.	.	} Not determined	} Not determined
TiO ₂ .	%	.	.	.		
Cr ₂ O ₃ .	%	.	.	.		

The results obtained are given in Table VII. They show clearly that the effect of using the methanol as received is to obtain an increased iron oxide value, the other constituents remaining practically constant. The increase in the iron oxide value is rather in excess of the anticipated amount and is possibly connected with other impurities in the alcohol. In this connection it should be stated that the methanol (as received) used in the above tests was of a pale yellow colour and contained a small amount of solid matter which was filtered off prior to use. Whilst all supplies have not these undesirable characteristics (*see* reference above to a recent consignment), the above tests show that it would be unwise to omit the distillation of the methanol prior to use, especially if there is no check on the density.

The density of three samples of methanol received from the Central Research Department was measured at the National Physical Laboratory. The results are as follows :

Methanol—	Density. G. per ml.	Methanol. %.
As received	0.7920	99.71
One distillation over calcium	0.7918	99.78
Two distillations over calcium	0.7916 ₈	99.83

¹ Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 352 P.

Summary.

(1) By means of hydrometers it is possible to measure the "dryness" of methanol and control the effect of the distillation over calcium.

(2) If the methanol is up to a certain standard when received and is carefully stored, distillation over calcium may not be necessary, but if hydrometers are not available distillation is a safeguard.

(3) The presence of water in the methanol causes an increase in the percentage of iron oxide in the residue. The percentages of the other constituents, *viz.*, silica, oxide of manganese, alumina and phosphorus pentoxide, remain practically constant.

(4) Previous results which indicated an increase in the percentage of phosphorus pentoxide on the addition of water may have been due to the presence of dissolved oxygen.

The work described above was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research for the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

(e2) *Experiments on the Composition of Extracted Non-Metallic Residues from High-Carbon and -Phosphorus Steels.*¹

By G. E. SPEIGHT, B.Sc., A.I.C.

(Under the direction of T. Swinden, D.Met., Director of Research.)

SYNOPSIS.

The presence of phosphorus and iron oxides in the non-metallic residue extracted by the alcoholic iodine method from steels of high carbon and phosphorus contents is discussed. Observations are made on the power of carbon arising from the decomposition of iron carbide to adsorb constituents of the alcoholic iodine solvent.

Alcoholic iodine experiments demonstrating the presence of these contaminating oxides in the separated residue are reported. Whilst these results do not provide conclusive evidence of the validity of this adsorption theory, data are presented showing that the additional iron-oxide content is removed by an after-treatment of the non-metallic carbonaceous residue with ammonium tartrate solution. Complete removal of the phosphorus pentoxide contamination is not obtained by this treatment.

The paper concludes with an appendix showing the marked influence of carbon in promoting enhanced alumina contents in residues from a high-carbon steel having an aluminium addition equivalent to 2.5%. The ammonium tartrate after-treatment removes the excessive alumina contamination of these residues.

Review of Previous Work.

The presence of a small but definite amount of phosphorus

¹ A communication from the Central Research Department, The United Steel Companies, Ltd. (Stocksbridge, Sheffield), received February 18, 1943.

pentoxide in the non-metallic residue extracted from steel and cast iron by the alcoholic iodine method has long received the attention of operators of the residue methods. While the reason for the occurrence of this oxide is not clear, reference to many results given in previous Reports shows that it cannot be regarded as an oxygen-bearing constituent of the steel.

The reduction of phosphorus pentoxide has been shown by Sloman to be complete under the conditions of the vacuum fusion process, hence its presence in the non-metallic residue must, therefore, be regarded as an undesirable feature of the method of separation.

The problem has been closely studied by the Oxygen Sub-Committee and many references are to be found in previous Reports. In an examination of an acid open-hearth cast by Bramley, Maddocks and Tateson,¹ alcoholic iodine determinations are reported on a series of steel bath samples of carbon content decreasing from 1.31% to 0.24% with a constant phosphorus content of 0.028%. Their results showed that, with samples of high carbon content, *i.e.*, over 0.6%, residues of high ferrous-oxide content were obtained, and that, in general, the content of phosphorus pentoxide in the residue decreased with decreasing carbon content. Since it is inconceivable that such high ferrous-oxide concentrations occur in steel containing between 1.3% and 0.7% of carbon, the authors concluded that dissolution of the iron carbide was incomplete and that, on ignition of the residue, the residual carbide was converted to oxide. Circumstantial confirmation of this conclusion was given by comparison of the calculated oxygen content (*i.e.*, SiO_2 , FeO , MnO , Al_2O_3) with that obtained by the vacuum fusion method. Those authors' conclusion regarding the occurrence of phosphorus pentoxide in the alcoholic iodine residues was that a close relationship existed between the iron-oxide content of the residue and the phosphorus-pentoxide content of the slag.

Work on this aspect of the alcoholic iodine method was continued at Sheffield University,² and, although the results of this later examination were not published, some interesting observations were made. The iron-oxide fraction of the residue was abnormally high when the carbon content of the steel was greater than 0.45%, and also bore some relation to the heat-treated condition of the sample; quenched specimens gave higher values than normalised specimens. In addition, it appeared that the phosphorus-pentoxide content of the ignited residue also was closely related to the heat-treated condition.

Concurrently with the research at Sheffield University, Taylor-Austin,³ using both the alcoholic iodine and the aqueous iodine

¹ Eighth Ingot Report, *loc. cit.*, p. 11.

² Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 380 p.

³ Eighth Ingot Report, *loc. cit.*, pp. 159, 121.

methods with particular reference to pig and cast irons, also encountered the interference of these two oxides. With phosphoric pig irons the alcoholic iodine method gave residues of extremely high iron-oxide and phosphorus-pentoxide contents, although an increased stirring time of 48 hr. reduced these concentrations. Similar experiments on a steel of very low carbon and high phosphorus (1.48%) content gave a residue containing a normal iron-oxide content (0.020%) but an extremely low phosphorus-pentoxide concentration (0.0015%). Thus, while in the absence of carbon almost complete decomposition of iron phosphide is obtained, the presence of large amounts of iron carbide, as in cast iron, leads to residues having large concentrations of phosphorus pentoxide. Further experiments, to investigate the effect of increased water content of the methanol, suggested a possible explanation of the behaviour of phosphides in the alcoholic iodine method, namely, that part of the phosphide is decomposed by iodine and converted to phosphate by interaction with water, the residue containing ultimately mixed iron phosphide and phosphate. Treatment of the residue with ammonium-citrate solution removed a large part of the phosphorus contamination, leaving a residue with ferrous-oxide and phosphorus-pentoxide contents conforming to the formula Fe_3P .

The same author's work ¹ with the aqueous iodine method of separation showed that, with pig iron, partial hydrolysis of iron phosphide occurred, yielding a residue with an excess of iron phosphate. Subsequent treatments with ammonium citrate removed this excess of phosphate, but that remaining as iron phosphide was unattacked, being dissolved by other treatments. It was also concluded that iron carbide was only partially decomposed during the initial attack by aqueous iodine, but treatment with ammonium citrate completely removed the remaining small amount.

Rooney ² reported the small interference of phosphorus in the alcoholic iodine method, and suggested that, while the method was suitable for low- and medium-carbon steels (under 0.43% of carbon), the method was not suitable for higher-carbon steels, owing to the low solubility of iron carbide in alcoholic iodine. The deoxygenating treatment and the use of disc samples were considered to affect the quantity of phosphorus pentoxide retained by alcoholic iodine residues. It is noteworthy that the chlorine method of extraction, usually, gives residues of lower phosphorus-pentoxide content than does the alcoholic iodine method.

The position may therefore be summarised as follows: In the ignited residue of the usual alcoholic iodine procedure, ferrous oxide and phosphorus pentoxide occur to an extent which depends largely on the carbon content of the steel. There is evidence that much of

¹ Taylor-Austin, Eighth Ingot Report, *loc. cit.*, p. 123; Third Report of the Oxygen Sub-Committee, *loc. cit.*, p. 358 P.

² Rooney, Eighth Ingot Report, *loc. cit.*, p. 156; Third Report of the Oxygen Sub-Committee, *loc. cit.*, p. 349 P.

the phosphorus contamination exists as oxide in the unignited residue from pig and cast irons. Calculation of the oxygen content shows that these oxides do not occur as such in the original material, since in many cases the oxygen content of the phosphorus pentoxide alone exceeds the total oxygen as determined by the vacuum fusion method.

Explanations Regarding the Occurrence of Iron Oxide and Phosphorus Pentoxide in Alcoholic Iodine Residues.

These facts have been widely discussed by the Sub-Committee with, naturally, opposing opinions. It is felt by some Members that the carbides and phosphides of iron are not completely decomposed, and that ignition of the residue containing the undecomposed compounds produces iron oxide and phosphorus pentoxide. In the author's opinion, the facts can be explained by a theory postulating complete decomposition of both carbide and phosphide. While this explanation is not necessarily complete, the author believes that it meets more fully the experimental data presented in the foregoing introductory review.

It is suggested that alcoholic iodine reacts with the steel, decomposing the carbides and phosphides of iron to yield soluble iron iodide, free carbon and phosphorus, which latter dissolves in the solvent as either elemental phosphorus or phosphorus iodide. The dissolved phosphorus (or phosphorus compound) is then hydrolysed by a small trace of water, either contained initially in the alcohol or formed subsequently during reaction of the iodine/alcohol solvent with the steel, yielding an oxide or oxy-acid of phosphorus. (The agency of water for the above reactions is suggested for simplicity, but, since alcohol itself is a weakly ionizing liquid, the reactions might well occur in the complete absence of water.)

Since it is well known that certain forms of carbon possess large adsorptive powers in both gaseous and liquid media, it is conceivable that the voluminous free carbon deposit, resulting from the breakdown of iron carbide in high-carbon steels, also has adsorptive properties. Under such circumstances, the free carbon adsorbs iron and phosphoric oxides either as compounds or as ions, so that, on filtering the residue, varying quantities of iron and phosphorus are simultaneously separated. Moreover, other soluble constituents of the alcoholic iodine solvent, *e.g.*, aluminium and silicon compounds, may undergo separation with the free carbon in a similar manner. If this is a true adsorptive effect, extra washing or treatment with either alcohol or alcoholic iodine will effect little removal of the adsorbed substance. On the other hand, an after-treatment of the separated residue with a solution of entirely different chemical characteristics will substantially modify the quantity of adsorbed substance. Many similar examples in analytical chemistry are well known.

The main inference of this explanation is that the adsorptive effect would be operative in alcoholic iodine determinations on all steels. Naturally, the effect would be at a maximum in determinations on steels of high carbon contents and, moreover, more phosphorus pentoxide would occur in ignited residues from high-phosphorus steels than from low-phosphorus steels of equal carbon content. At the same time, the quantitative result of the adsorption would not be absolutely constant for a given carbon and phosphorus content, but would be influenced by slight local variations in the test conditions, *i.e.*, the heat-treated condition of the sample, the water content of the alcohol, the temperature of the reaction and the weight and form of the sample under examination.

The experimental facts quoted earlier conform to this explanation. The furnace samples examined by Bramley, Maddocks and Tateson and the subsequent work on carbon and phosphorus at Sheffield University, in which separated residues were subjected to extra treatment with alcoholic iodine, but with little removal of iron and phosphorus contamination, support this view. Indeed, one of the above authors' conclusions was that a relationship existed between the heat-treated condition of the sample and the extent of the oxide contamination. Taylor-Austin's work on both steel and cast iron illustrates the effect of the presence of very high and low carbon contents and also the decreased contamination resulting from treatment of the residue with a solution of different chemical characteristics (*e.g.*, ammonium citrate). The present author attributes this improvement to a reduction in the adsorptive power of the carbon. The explanation is supported by Rooney's statement that the alcoholic iodine method is suitable for low- and medium-carbon steels; with steels of normal phosphorus contents, a carbon figure of about 0.4% is necessary before the adsorption and subsequent contamination with iron and phosphorus oxides become of really reasonable dimensions. However, the theory does not exclude the possibility of insoluble iron phosphide in extracted residues, when the phosphide is associated in the material by direct union with other non-metallic inclusions insoluble in alcoholic iodine. The author believes that such possibilities exist, particularly in phosphoric pig and cast irons, in which there is evidence of the association of titanium and phosphide inclusions. Finally, in the chlorine extraction method, which is a "dry" reaction, the adsorptive effect of the separated carbon will be less evident and subsequent contamination is on a much lower scale.

Experimental Data.

Whatever may be the true cause of the occurrence in alcoholic iodine residues of iron and phosphorus oxides, contamination undoubtedly exists, and if the alcoholic iodine method is to serve as a satisfactory basis for the determination of non-metallic inclusions

(and presumably of oxygen) in steel, then devices must be sought to remove this undesirable feature.

With this object in view, the following experiments were carried out, and, whilst the work is far from complete and does not arbitrate between the two explanations, it does show that the excessive contamination of normal residues can be reduced considerably by the principle of after-treatment.

TABLE VIII.—*Analysis of the Steels Examined.*

Steel.	Carbon. %.	Manganese. %.	Silicon. %.	Sulphur. %.	Phosphorus. %.
4104 (high-carbon, high-phosphorus)	1.08	0.40	0.175	0.019	0.113
4105 (high-carbon, low-phosphorus)	1.06	0.37	0.15	0.018	0.019
4360 (low-carbon, high-phosphorus)	0.11	0.30	0.09	0.024	0.092

For simplicity, three steels only were examined in the annealed condition. Other compositions and heat-treated conditions may be examined later, if considered necessary. The selected compositions were made in an 18-lb. spark-gap high-frequency furnace, using a sillimanite lining. Samples of each forged bar were dispatched to Mr. C. W. Short, of Messrs. John Lysaght, Ltd., and Mr. T. E. Rooney, of the National Physical Laboratory, who have kindly co-operated in much of the experimental work. The type and analyses of the three steels are given in Table VIII.

Determination of Oxygen by the Vacuum Fusion Method.

Direct determinations of oxygen by the vacuum fusion method were carried out to provide total oxygen reference figures for com-

TABLE IX.—*Oxygen Content of the Steels Examined.*

Sample.	Laboratory.*	Oxygen. %.	Hydrogen. ML. per 100 g.	Nitrogen. %.
4104	C.R.D.	0.005 ₅	0.8	0.003 ₅
	N.P.L.	0.004	Trace	0.003 ₅
4105	C.R.D.	0.005	0.5	0.003
	N.P.L.	0.004	Trace	0.003 ₅
4360	C.R.D.	0.025	0.2	0.003 ₅
	C.R.D.	0.023 ₅	0.3	0.004
	N.P.L.	0.024	0.1	0.003

* C.R.D. = Central Research Department, The United Steel Companies, Ltd. N.P.L. = National Physical Laboratory.

parison with those obtained by the residue methods. The results given in Table IX. agree with the expected oxygen contents for these types of steel; the two high-carbon steels have a low oxygen content of 0.004–0.005%, whilst the low-carbon steel contains considerably more oxygen, 0.024%.

Microscopical Examination.

Sections of the three steels (annealed at 650° C. for 1 hr. and furnace-cooled) were examined microscopically in both the unetched and etched conditions. The high-carbon steels, Nos. 4104 and 4105, had very similar features. In the unetched condition, uniform distribution of small elongated monophase sulphides and small particles of alumina and silicates, with complete absence of stringer inclusions, was observed. In the etched condition, these steels showed a banded structure, more marked in the high-phosphorus steel 4105, consisting of dense sorbitic pearlite with minute areas of cementite in a partial network pattern.

The low-carbon steel, 4360, was markedly dirtier than the two high-carbon materials. The distribution of inclusions was uniform, comprising small particles of alumina and silicates with small elongated sulphides. Larger streak inclusions, mainly of silicates of aluminium, were occasionally observed. The etched microsection showed a slight banded structure of small ferrite crystals with small areas of partially spheroidised sorbitic pearlite.

Extraction of Non-Metallic Inclusions by the Chlorine Method.

Specimens of these steels were submitted to the chlorine extraction method ¹ by Mr. Short, with the results shown in Table X.

Comparison of the chlorine results with the direct oxygen values by vacuum fusion indicates that one or more constituents of the residue are in excess. The immediate conclusion is that the iron-oxide value is too high and consequently does not occur in the original sample. Neglecting the oxygen equivalent due to this iron oxide (and, of course, that due to phosphorus pentoxide), the sum of the oxygen contributed by the remaining oxides is of a more comparable character. Comparison of these results with the alcoholic iodine results (*see* later) also suggests that the values for manganous oxide are slightly high. The oxygen content of these steels can be accounted for by consideration of the oxygen equivalents of the silica and alumina alone.

The phosphorus-pentoxide contents are comparatively low, showing that contamination, whatever its cause, is very slight in the chlorine method. Thus, while these chlorine extraction results are somewhat on the high side and are perhaps not entirely representative, the presence of high carbon and phosphorus in steel does not

¹ Colbeck, Craven and Murray, Third Report of the Oxygen Sub-Committee, *loc. cit.*, p. 332 P; Eighth Ingot Report, *loc. cit.*, p. 109.

TABLE X.—*Extraction of Non-Metallic Inclusions by the Chlorine Method from High-Carbon Steels 4104 and 4105.*

Experiments at Messrs. John Lysaght, Ltd.

Form of sample : 2-mm. slices. Chlorination temperature : 500° C. Duration of tests : 4 hr.				
	No. 4104.		No. 4105.	
	Oxide. %.	Oxygen. %.	Oxide. %.	Oxygen. %.
Total ignited residue.	0.073 ₅	...	0.057 ₅	...
Analysis of residue as percentage of steel :				
SiO ₂	0.007	0.004	0.004	0.002
FeO	0.038	0.008	0.031	0.007
MnO	0.006	0.001	0.008	0.002
Al ₂ O ₃	0.004	0.002	0.005	0.002
TiO ₂	Trace		Trace	
Cr ₂ O ₃	N.D.		N.D.	
P ₂ O ₅	0.012		0.003	
Total oxygen		0.015		0.013
Total oxygen by vacuum fusion		0.005		0.004 ₅

result in very pronounced contamination of the non-metallic residue. It must be pointed out that, owing to the high carbon content of these steels, the sample did not disintegrate completely during chlorination; consequently, the washing of the residue after chlorination was a difficult operation, and may have contributed to the high iron-oxide result.

Extraction of Non-Metallics by the Alcoholic Iodine Method.

Alcoholic iodine extractions were carried out by two co-operating laboratories. The precise procedures differed slightly, one operator using the standard stirring method ¹ with de-aeration of the alcohol, the other the simplified boiling method.² The results show certain differences, due no doubt to slight variations in technique, and on this account it is desirable to consider the results individually.

(a) *Experiments at the National Physical Laboratory.*

Table XI. gives results obtained by Mr. T. E. Rooney. Comparison of the oxygen results by alcoholic iodine with those by the vacuum fusion method shows clearly that the iron and phosphorus oxides found in the ignited residue are not oxygen-bearing con-

¹ Rooney, Second Report of the Oxygen Sub-Committee, 1939, Eighth Ingot Report, *loc. cit.*, p. 142.

² Stevenson and Speight, Third Report of the Oxygen Sub-Committee, *loc. cit.*, p. 352 P.

stituents of the steel. Indeed, if the oxygen equivalents of these oxides are omitted, the oxygen content contributed by the remaining oxides bears comparison with the vacuum fusion results.

TABLE XI.—*Extraction of Non-Metallics by the Alcoholic Iodine Method.*

Experiments at the National Physical Laboratory.

Form of sample : 1-mm. discs. Weight of sample : 10 g. Method : Standard stirring method. Time of stirring : No. 4104, 12½ hr.; No. 4105, 9½ hr.				
	No. 4104.		No. 4105.	
	Oxide. %.	Oxygen. %.	Oxide. %.	Oxygen. %.
Total ignited residue . . .	0.115	...	0.066 ₅	...
Analysis of residue as percent- age of steel :				
SiO ₂	0.006	0.003	0.005	0.002 ₅
FeO	0.050	0.011	0.028 ₅	0.006 ₅
MnO	Trace	...	0.002	0.000 ₅
Al ₂ O ₃	0.009 ₅	0.004 ₅	0.007 ₅	0.003 ₅
Cr ₂ O ₅	0.005 ₅		0.006 ₅	
P ₂ O ₅	0.036 ₅		0.015	
Total oxygen		0.018 ₅		0.013
Total oxygen by vacuum fusion		0.005		0.004 ₅

The stirring times for these determinations were very long, and dissolution of the sample was very difficult, owing to the formation of a dense layer of carbon round the metal. Although the rapid stirring employed assisted in breaking down this carbon layer, there was undoubtedly some measure of protection, and a few discs tended to retain their original shape. However, stirring was prolonged until no magnetic material remained. This phenomenon, whereby the sample tended to retain its original shape and form, renders conditions ideal for adsorptive influences, since the alcoholic iodine must act through the carbon layer to extract the iron.

The results shown in Table XI. are typical of alcoholic iodine determinations on high-carbon materials.

(b) *Experiments at Central Research Department, The United Steel Companies, Ltd.*

(1) *Results Obtained with the Simplified Boiling Method.*—Initial experiments soon disclosed the occurrence of the protective carbonaceous layer, resulting in the extracted residue having the identical appearance of the metal sample. It was obvious, therefore, that a residue of such a form could not be washed satisfactorily in the usual manner. Consequently, after filtering, these residues were

crushed under alcohol and allowed to stand for 3 hr. before they were again filtered and finally washed with alcohol. The results were variable, ranging between 0.098% and 0.279% total ignited residue for steel 4104, and between 0.065% and 0.125% for steel 4105, the bulk of the residue being iron oxide. It was concluded that undecomposed metal still remained in the residue after the 12-hr. extraction period, and that a further treatment with alcoholic iodine on the crushed residue would be of advantage.

The results recorded in Table XII. were obtained. They agree closely with those in Table XI.; the iron- and phosphorus-oxide

TABLE XII.—*Extraction of Non-Metallics by the Alcoholic Iodine Method.*

Experiments at Central Research Department, The United Steel Companies, Ltd.

Form of sample : 2-mm. discs. Weight of sample : 16 g. Method : Simplified boiling method. Boiling time : 12 hr.				
	No. 4104.		No. 4105.	
	Oxide. %.	Oxygen. %.	Oxide. %.	Oxygen. %.
Total ignited residue . . .	0.093	...	0.074	...
Analysis of residue as percent- age of steel :				
SiO ₂	0.005	0.002 ₅	0.006	0.003
FeO	0.034	0.007 ₅	0.031	0.007
MnO	0.001	0.000 ₂	0.001	0.000 ₂
Al ₂ O ₃	0.008	0.003 ₈	0.007	0.003 ₃
P ₂ O ₅	0.031		0.016	
Total oxygen		0.014		0.013 ₅
Total oxygen by vacuum fusion		0.005		0.004 ₅

contamination and the agreement with the vacuum fusion result if these oxides are omitted from the summation are similar.

(2) *Experiments on the After-Treatment of Residues.*—Attempts were now made to remove the iron-oxide contamination of the residue. The following four residue treatments were investigated, concentrating on steel 4104 (*i.e.*, high-carbon and -phosphorus) after 12 hr. boiling with 10% alcoholic iodine :

(a) The residue was dried, crushed and boiled for 3 hr. under a reflux condenser with anhydrous methyl alcohol, being finally allowed to stand overnight, filtered, alcohol-washed and ignited.

(b) The residue was dried, crushed and treated for 3 hr.

under a reflux condenser with boiling 10% alcoholic iodine solution, followed by the standing period, filtration, &c., as in (a) above.

(c) The residue was dried, crushed and treated for 3 hr. under a reflux condenser with 10% ammonium-tartrate solution, followed by standing overnight, filtering and washing with 10% ammonium tartrate.

(d) The residue, consisting of whole discs of carbonaceous matter, was transferred without drying to the reflux condenser and boiled with 10% ammonium tartrate for 3 hr., the determination being completed as in (c) above.

TABLE XIII.—*Results Obtained by the Treatment of Alcoholic Iodine Residues from Steel 4104.*

Experiments at Central Research Department, The United Steel Companies, Ltd.

Treatment of Residue.	Total Ignited Residue. %.	Analysis of Residue.			Analysis of Wash Solution.	
		SiO ₂ . %.	FeO. %.	P ₂ O ₅ . %.	FeO. %.	P ₂ O ₅ . %.
(a) Boiling alcohol for 3 hr.	0.066 0.072	0.007 0.008	0.015 0.024	0.027 0.032	0.018 0.011	0.002 0.001
(b) Boiling 10% alcoholic iodine for 3 hr.	0.075 0.435	0.007 0.007	0.023 0.345	0.025 0.030	0.012 0.270	0.005 ...
(c) Boiling 10% ammonium tartrate for 3 hr.	0.118 0.119	0.005 0.006	0.063 0.065	0.027 0.026
(d) Boiling 10% ammonium tartrate for 3 hr. Residue <i>not</i> dried and crushed prior to treatment.	0.053 0.060	0.006 0.006	0.008 0.009	0.020 0.022	0.059 0.150	0.013 0.010

The various residues and treatment solutions were analysed for iron and phosphorus, with the results given in Table XIII. The following comments are made on these figures :

(1) Had the residues not been treated, the total ignited residues would have been very variable, as exemplified by the duplicates of modifications (d) and (b). Thus, the formation of the protective carbon layer is a very prominent and real obstacle.

(2) The most marked effect is given by modification (d), in which the residue was treated with 10% ammonium tartrate. This development is not unexpected, since this solution, being chemically very different from the original alcoholic iodine solvent, would exert a larger effect on the basis of the adsorption theory than would the remaining solutions tested.

(3) The difference in the results of treatments (c) and (d) is surprising, since it was considered that treatment (c) would be more effective than (d). It can only be concluded that the extra manipulation involved in crushing the residue, during which time it air-

dries, results in slight atmospheric oxidation of the contaminating iron and subsequent failure to remove it by the ammonium tartrate.

(4) The second most effective treatment is modification (a), i.e., boiling alcohol, but it is probable that, given equal initial decomposition by the alcoholic iodine, very little difference would be observed between the efficiency of alcohol and alcohol-iodine solution as treatment solutions. It is, however, quite apparent that the residues from high-carbon steels must be given some after-treatment, if only to ensure efficient washing.

(3) *Application of the After-Treatment to the Three Experimental Steels.*—Comparative determinations, using the simplified boiling method, were now made on the three steels 4104, 4105 and 4360. The after-treatment with ammonium tartrate was adopted, and, for the reason stated in paragraph (4) above, similar tests were made incorporating the alcohol after-treatment. Table XIV. gives the results obtained; the following comments are made on these results :

(1) The total ignited residue value, in every case, is reduced by the ammonium-tartrate treatment.

(2) Considering the effect of the after-treatment on the individual constituents :

(a) The silica value is slightly reduced.

(b) The iron-oxide content is substantially reduced in the case of 4104 and 4105 and only slightly with 4360, and, in the author's opinion, the lower results are the more accurate for materials of this type. Steels 4104 and 4105 are of high carbon content, and on the basis of purely theoretical reasoning they might be expected to have low ferrous-oxide contents. Steel 4360 is of low carbon content, hence its ferrous-oxide content should be correspondingly higher.

(c) The low-carbon steel 4360 only shows an appreciable manganese-oxide content, on which the ammonium-tartrate treatment appears to have no effect. This result is to be expected, since the non-metallic inclusions in this steel consist of ferrous and manganese-aluminium silicates, stable to ammonium tartrate.

(d) The alumina content of the two high-carbon steels is slightly reduced, whilst that of 4360 is unaffected.

(e) The reduction in phosphorus-pentoxide content is not entirely satisfactory, suggesting that, in this connection, ammonium tartrate is not ideal for the after-treatment.

(f) If the phosphorus-pentoxide content is ignored, the calculated oxygen contents of the residue after treatment are in closer agreement with the oxygen contents determined by vacuum fusion.

TABLE XIV.—*Extraction of Non-Metallic Inclusions by the Alcoholic Iodine Method. Comparative Results by Alcohol and Ammonium-Tartrate After-Treatments.*

Experiments at Central Research Department, The United Steel Companies, Ltd.

Sample and Details of Method Used.	Total Ignited Residue, %.	Analysis of Ignited Residue as a Percentage of the Steel.										Total Oxygen. %.	
		SiO ₂ .		FeO.		MnO.		Al ₂ O ₃ .		P ₂ O ₅ , %.	Alcoholic Iodine.	Vacuum Fusion.	
		SiO ₂ , %.	O ₂ , %.	FeO., %.	O ₂ , %.	MnO., %.	O ₂ , %.	Al ₂ O ₃ , %.	O ₂ , %.				
4104 (high-carbon, high-phosphorus): (a) Refluxed with 10% ammonium tartrate. (b) Residue crushed under alcohol and refluxed with alcohol.	(1) 0.042	0.006	0.0032	0.006	0.0013	0.001	0.0002	0.007 ₈	0.0035	0.020	0.008	} 0.005	
	(2) 0.032	0.005	0.0027	0.001	0.0002	Trace	Trace	0.007	0.0033	...	0.006		
	(1) 0.080	0.008	0.0043	0.022	0.0049	0.001	0.0002	0.009 ₈	0.0045	0.029	0.014		
	(2) 0.074	0.008	0.0043	0.023	0.0051	Nil	Nil	0.009	0.0042	...	0.013 ₈		
4105 (high-carbon, low-phosphorus): (a) As above. (b) As above.	(1) 0.028	0.004	0.0021	0.006	0.0013	Nil	Nil	0.007	0.0033	0.009	0.006 ₈	} 0.004 ₈	
	(2) 0.024	0.004	0.0021	0.001	0.0002	Nil	Nil	0.007	0.0033	...	0.005 ₈		
	(1) 0.060	0.006	0.0032	0.018	0.0040	Nil	Nil	0.010	0.0047	0.014	0.012		
	(2) 0.048	0.007	0.0037	0.017	0.0038	Nil	Nil	0.008	0.0038	...	0.011 ₈		
4360 (low-carbon, high-phosphorus): (a) As above. (b) As above.	(1) 0.062	0.032	0.0171	0.009	0.0020	0.010	0.0022	0.006 ₈	0.0031	0.002 ₈	0.024 ₈	} 0.024	
	(2) 0.052	0.028	0.0149	0.005	0.0011	0.009	0.0020	0.006	0.0028	...	0.021		
	(1) 0.084	0.036	0.0192	0.015	0.0033	0.011	0.0024	0.006 ₈	0.0031	0.006	0.028		
	(2) 0.073	0.037	0.0197	0.012	0.0027	0.010	0.0022	0.006 ₈	0.0031	...	0.027 ₈		

(g) The three steels 4104, 4105 and 4360 illustrate clearly the joint effect of carbon and phosphorus in the alcoholic iodine method. Considering the results obtained under modification (b), it can be stated that :

(i) Given equal carbon contents, the extent of phosphorus-oxide contamination depends on the phosphorus content of the steel. Iron-oxide contamination is similar with equal carbon content.

(ii) With unequal carbon contents but equal high-phosphorus contents, a larger phosphorus-oxide constituent occurs in the residue from the higher-carbon steel. Similarly, a larger amount of iron oxide is found in the residue from the steel of higher carbon content.

Summary and Conclusions.

From the results of this, as yet incomplete, examination of the interference of high carbon and phosphorus contents in the alcoholic iodine method, the author is of the opinion that adsorption of the iron and phosphorus compounds by separated carbon plays a major part. It is possible that separation of undecomposed carbide and phosphide may occur, as suggested by other workers on the Subcommittee. The effective use of after-treatment by alkaline tartrate solution, however, is more indicative of the former reason for the contamination of the residue which undoubtedly occurs with this class of steel. The use of tartrate treatment may be suggested as having, to a large extent, overcome the iron-contamination trouble. Further work is required before the phosphorus contamination is eliminated, and it is possible that alkali treatment, i.e., with dilute sodium carbonate solution or some similar reagent, may prove to be equally satisfactory for this purpose.

Appendix.—The Occurrence of Alumina in Ignited Alcoholic Iodine Residues.

In Section II., Part A(e3), Rooney describes experiments by the alcoholic iodine method on three steels with aluminium and nitrogen contents varying between 0.145% and 0.67% and between 0.0045% and 0.0125%, respectively. It was found that after ignition each of the separated residues contained a quantity of alumina far in excess of that present as such in the steel, assuming that the oxygen content, determined by the vacuum fusion method, existed entirely as alumina. Evidence is also presented showing that, in addition to the alumina constituent of the steel, other aluminium compounds such as carbide and nitride are separated by the alcoholic iodine method and converted to oxide on ignition. Methods of analysis, whereby the true alumina can be separated from that arising from the ignition of other aluminium compounds, are described. The

oxygen contents obtained by consideration of the true Al_2O_3 only are reasonably comparable with the vacuum fusion results.

In this connection, experiments carried out by the author are of interest. The simplified boiling method was applied to a series of synthetic samples, the equivalent aluminium content of each test being 2.5%; the determinations were designed to study the effect of carbon on the alumina content of the separated residues. The samples were composed of iron discs and aluminium sheet as follows:

(1) 10 g. of oxygen-free iron (N.P.L. iron, Mark 2) together with 0.25 g. of special-purity aluminium.

(2) 10 g. of steel 4105 with an addition of 0.25 g. of aluminium, the residue being refluxed with alcohol.

(3) 10 g. of steel 4105 with an addition of 0.25 g. of aluminium, treated afterwards with ammonium-tartrate solution.

Treatment of the ignited residue as described in Section II., Part A(e3), method (2), by sulphuric acid to differentiate between truly-occurring alumina and that produced by ignition of other aluminium compounds, was applied.

The results given in Table XV. were obtained. They show very

TABLE XV.—*Tests on Ignited Alcoholic Iodine Residues.*

Experiment.	Total Ignited Residue. %.	Analysis of Residue.			Al ₂ O ₃ Content of Solution after Treat- ment. %
		SiO ₂ . %.	Al ₂ O ₃ . %.		
			Insoluble.	Soluble.	
(1) N.P.L. iron (Mark 2) (0.01%) + 0.25 g. metallic aluminium .	0.007	Nil	Nil	0.005 _s	...
(2) Steel 4105 (0.1.06%) + 0.25 g. metallic aluminium :					
(a) Residue refluxed with alco- hol for 3 hr.	0.081 0.098	0.004 0.004	0.004 0.006	0.036 0.037	0.005 0.008
(b) Residue refluxed with 10% ammonium tartrate for 3 hr.	0.088	0.005	0.005	0.006	0.042

clearly a relationship between the carbon content of the sample and the alumina content of the alcoholic iodine residue. With the almost complete absence of carbon, as in the first experiment, a small quantity of alumina, soluble in sulphuric acid, is found. In the presence of 1.06% of carbon, the same addition of aluminium results in an increased alumina content of the residue, the bulk of this alumina being soluble in sulphuric acid. Reference to the alcoholic iodine determinations on this steel in the absence of aluminium (Table XIV.) indicates that this excessive alumina content could not have arisen from steel 4105. Experiment (1),

Table XV., shows the absence of other aluminium compounds in the special-purity aluminium. Consequently, the effect arises from the combined presence of voluminous carbon from decomposed iron carbide and soluble aluminium compounds, and the aluminium contamination is probably due to adsorption. Treatment of a similar unignited residue with 10% ammonium-tartrate solution almost completely removes this acid-soluble alumina constituent, which reappears in the wash solution.

Fortunately, in most steels the carbon and aluminium contents are much less than those of the above synthetic sample 4105. Although with these concentrations the adsorptive effect is not too excessive, it will, however, be operative in more normal steels. Its effect can be noticed in the three aluminium steels examined by Rooney, particularly steel No. 2 containing 0.285% of carbon and 0.67% of aluminium. Residues from these three steels were treated with 3% sodium-carbonate solution and 5% hydrochloric acid before ignition in an endeavour to remove aluminium nitride. This treatment did, in fact, remove certain quantities of aluminium from the separated residues, and calculation of the nitrogen equivalent of this soluble alumina gave the results quoted in Table XVI. They show that, whilst for samples Nos. 1 and 3 the alkali-soluble alumina is explicable on the basis of nitride, sample No. 2 has a soluble-alumina content in excess of that associated as nitride. It is significant that this steel has the highest aluminium content.

TABLE XVI.—*Comparison of Soluble Alumina and its Nitrogen Equivalent with the Nitrogen Content of the Steel.*

Steel.	Alumina Soluble in Sodium-Carbonate Solution. %.	Nitrogen Equivalent of Soluble Al_2O_3 . %.	Nitrogen Content of Steel. %.
No. 1 (0.15% Al) . .	0.020	0.005 ₅	0.006 ₅
No. 2 (0.67% Al) . .	0.029 ₅	0.008 ₁	0.004 ₅
No. 3 (0.17% Al) . .	0.050 ₅	0.014 ₁	0.012 ₅

Conclusion.—The results of this short examination show that, whilst the alcoholic iodine method may separate other compounds beside oxide, such as nitride and/or carbide, the possibility of carbon-adsorbed aluminium must not be overlooked. Removal of the adsorbed aluminium may be effected by after-treatment of the separated residue with a suitable solvent of different chemical characteristics.

The author is pleased to acknowledge the assistance of his colleague, Mr. D. J. D. Unwin, who carried out, with great care, many of the experiments described in this paper.

(e3) *The Examination and Analysis of Residues from the Alcoholic Iodine Method.*¹

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(Under the direction of C. Sykes, D.Sc., F.R.S.)

SYNOPSIS.

Experiments have been made on residues from the three aluminium steels of the Oxygen Sub-Committee's alloy-steel series in order to determine whether it is possible to differentiate between alumina contained in the steel as such and aluminium in the form of carbide or nitride.

Reference is made to experiments with aluminium carbide in alcoholic iodine solution.

The possibility of iodine residues containing aluminium carbide and/or nitride was referred to in the Third Report of the Oxygen Sub-Committee² and it was hoped that some evidence of the existence of these compounds could be derived from residues obtained from the three specially prepared aluminium steels (see Section III.(h)).

An X-ray examination gave negative results, but a chemical determination on the residue from steel No. 3 (aluminium 0.15%, nitrogen 0.01%) yielded 0.005% (on the weight of steel used) of nitrogen, indicating the presence of undecomposed nitride.

It has been suggested that aluminium carbide should be easily decomposed in iodine solution. There is some evidence, however, that this is not the case. A piece of aluminium containing an appreciable amount of aluminium carbide, according to an X-ray examination, was stirred with alcoholic iodine solution at room temperature. The temperature rose to 31° C., but the reaction was not violent. The stirring was continued for 2½ hr. A piece of the material still remained together with a yellowish-brown powder and some smaller grey pieces. An X-ray examination indicated that the yellow powder was aluminium carbide, but aluminium lines given by the original sample were absent. The small grey pieces consisted of aluminium carbide plus graphite. The larger piece of material remaining was stirred with a fresh supply of hot iodine solution for 2 hr. More yellow powder was obtained together with some small pieces of partially decomposed material. There is thus evidence that the decomposition of massive aluminium carbide is slow and probably incomplete in alcoholic iodine solution. Also the results obtained on an iron-carbon alloy containing aluminium and only a small percentage of nitrogen (Third Report, Table XX.³) suggest that aluminium carbide may be contained in residues from aluminium steels.

¹ Received November 27, 1942.² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 347 p.³ *Ibid.*, p. 348 p.

Aluminium carbide or nitride in the residue will after ignition change to aluminium oxide. Thus the routine analysis of residues so contaminated will lead to oxygen values in excess of the true values as given by the vacuum fusion method, and this extra oxygen will be associated with high alumina values.

The Separation of Alumina from other Aluminium Compounds contained in Iodine Residues.

In the analysis of residues from the three aluminium steels a large proportion of alumina was found. The calculation of total oxygen from the percentage of alumina gave a value very much in excess of the total oxygen by the vacuum fusion method. The results are given in Table XVII.

For the separation of alumina from the other possible aluminium compounds or their oxidised products three methods were employed as follows :

Method (a).—The residue was ignited at a moderate temperature in order to remove free carbon and was then treated with sulphuric acid. It is probable that the aluminium compounds and any oxide produced from them during the ignition will be more easily soluble than the alumina originally present in the steel as such.

The residue was digested on a hot-plate with sulphuric acid (1 : 1) until the insoluble residue was white in colour. The mixture was evaporated to fumes, cooled, diluted, heated to boiling and filtered. Silica was determined in the ignited residue, which consisted mainly of alumina. The residue was examined for traces of iron and manganese. The other constituents of the residue, including the soluble aluminium compounds, were estimated in the filtrate.

Method (b).—The residue before ignition was washed free from iron iodide with alcohol and with hot water. Two washings were then made alternately with hot 3% sodium-carbonate solution and cold 5% hydrochloric acid. After a final wash with hot water, the filter was ignited. Aluminium nitride is stated to be soluble in alkalis, and aluminium carbide to be decomposed by water and to be soluble in acids (Van Nostrand's Chemical Annual, 1926, p. 182). The ignited residue was treated as in method (a) above.

Method (c).—The unignited residue was digested with 10 ml. of concentrated nitric acid on a hot-plate until the carbon and the filter paper were oxidised. In some cases a few millilitres of either hydrochloric or perchloric acid were added during digestion. When perchloric acid was added the mixture was evaporated to fumes. The mixture was diluted with hot water and filtered, and the residue was washed with hot 20% hydro-

TABLE XVII.—Oxygen Determinations on Three Aluminium Steels.

Steel No.	Type.	SiO ₂ *		FeO.		MnO.		Total Al ₂ O ₃ .		Total Oxygen. %.	
		%.	O ₂ %.	%.	O ₂ %.	%.	O ₂ %.	%.	O ₂ %.	Iodine Method.	Vacuum Fusion Method.
1	0.15% Al	0.063 0.058	0.002 0.0015	0.0065 0.007	0.0014 0.0016	Trace "	0.0485 0.046	0.0228 0.022	0.025 0.024	0.010
2	0.5% Al	0.078 0.082	0.0035 0.003	0.006 0.0075	0.0013 0.0016	0.0013 0.0014	0.0003 0.0003	0.059 0.065	0.028 0.032	0.031 0.035	0.010
3	0.15% Al, 0.01% N	0.097 0.105	0.0025 0.003	0.0085 0.008	0.0019 0.0017	Trace "	0.0705 0.084	0.033 0.040	0.036 0.047	0.007

TABLE XVIII.—Separation of Alumina from other Aluminium Compounds.

Steel No.	Type.	Method (a).		Method (b).		Method (c).	Laboratory.
		Insoluble Al ₂ O ₃ %.	Soluble as Al ₂ O ₃ %.	Insoluble Al ₂ O ₃ %.	Soluble as Al ₂ O ₃ * %.		
1	0.15% Al	0.0135 0.0125 0.019 0.018	0.035 0.0335 0.046 0.030 0.016 (1) 0.020 plus (2) 0.017 ...	0.028 0.028, 0.029	N.P.L. " J. Lysaght, Ltd. " " N.P.L.
2	0.5% Al	0.018 0.020 ... 0.014	0.0415 0.045 ... 0.057	... 0.021 (1) 0.0295 plus (2) 0.0035 ...	0.020 0.022 ...	" J. Lysaght, Ltd. N.P.L.
3	0.15% Al, 0.01% N	0.009 0.009 0.007	0.0755 0.065 0.065	... 0.010 (1) 0.0505 plus (2) 0.019 ...	0.019, 0.023 0.022, 0.023 ...	" J. Lysaght, Ltd. " " "

* (1) Soluble in Na₂CO₃ solution and HCl before ignition. (2) Soluble in H₂SO₄ after ignition.

chloric acid and finally with hot water. The filter was ignited and weighed, and silica was determined in the usual manner.

The results by the three methods are given in Table XVIII.

Method (b) was devised by Mr. Short, of Messrs. John Lysaght, Ltd., and the values for soluble alumina are given in two fractions; (1) is the fraction soluble in sodium carbonate and hydrochloric acid before ignition and (2) the fraction soluble in sulphuric acid after ignition of the residue. Mr. Short has calculated the nitrogen equivalents of fractions (1) and they are recorded below together with direct nitrogen determinations on the steel:

Steel No.	Al ₂ O ₃ . %. Fraction (1).	Nitrogen Equivalent. %.	Nitrogen in the Steel. %.
1	0.020	0.0055	0.0055-0.007
2	0.0295	0.0081	0.0045
3	0.0505	0.0141	0.010-0.0135

From these results, due allowance being made for the possibility of some nitride being decomposed during the iodine reaction, it seems probable that the soluble alumina is not all derived from aluminium nitride. Some proof of this is already afforded by nitrogen determinations on steel No. 3 at the National Physical Laboratory, which indicated that about 50% of the nitride was decomposed during the iodine reaction.

It will be noted under method (c) that after the alkali plus acid treatment (fraction (1)) an appreciable amount of alumina was soluble in sulphuric acid (fraction (2)) in the case of steels Nos. 1 and 3.

There is a possibility that the solubility in sulphuric acid (method (a)) may depend to some extent on the time of digestion, fineness of the particles, &c., so that the values for insoluble alumina by this method may be too low. This was the reason for the use of the third method (c), which gives higher values for insoluble alumina on steels Nos. 1 and 3. The higher values on steel No. 1 are in

TABLE XIX.—*Total Oxygen Contents of Three Aluminium Steels (Soluble Fraction of the Residue Neglected).*

Steel No.	Total Oxygen. %.			
	Method (a).	Method (b).	Method (c).	Vacuum Fusion Method.
1	0.0085, 0.0085 0.014, 0.0115	... 0.0115	0.013, 0.016	0.0085, 0.0125 0.013, fractional
2	0.012, 0.013 0.013	0.013, 0.014	0.0095, 0.0105
3	0.0095, 0.0075 0.0085, 0.0085	... 0.0095	0.012, 0.014	0.007, 0.009

agreement with the value obtained by the fractional vacuum fusion method.

Assuming that the soluble fraction of the residue is produced from compounds of aluminium originally present in the steel not as alumina, another set of oxygen values has been estimated in which the oxygen associated with this soluble fraction is neglected. The amended values are recorded in Table XIX.

Method (b) has been applied by Mr. Short in the analysis of the following three steels: No. 7 (3.5% nickel, 0.7% chromium); No. 8 (4.5% nickel, 1.25% chromium); No. 12 (18% chromium, 8% nickel). No manganese was found in the filtrate from the treatment with sodium carbonate, and a comparison of the analyses of steel No. 12 by the National Physical Laboratory and by Messrs. John Lysaght, Ltd., indicates that the treatment with sodium carbonate employed by the latter laboratory has no deleterious effects.

Summary.

(1) Experiments on a sample of aluminium containing aluminium carbide indicated that the decomposition of the carbide in alcoholic iodine solution is slow and may be incomplete even after prolonged treatment.

(2) The results of an examination of three aluminium steels by the iodine method showed that the percentage of alumina contained in the ignited residue gave a value for oxygen much in excess of the vacuum fusion value. A chemical determination of nitrogen on an unignited residue of steel No. 1 indicated that the residue contained undecomposed nitride.

(3) Experiments were made with three methods to distinguish between alumina separated from the steel as such and undecomposed or partially decomposed compounds of aluminium remaining in the residue. All three methods gave consistent results on steel No. 2 (0.5% aluminium) and the calculated value for total oxygen is in reasonable agreement with the vacuum fusion value. On steels Nos. 1 and 3 the results by the three methods are not so consistent; method (c) tends to give the highest results and with method (a) the results are somewhat scattered, but on the average are in reasonable agreement with the vacuum fusion values.

(4) Method (b) (treatment of the residue with sodium carbonate and dilute hydrochloric acid) has been successfully employed in the examination of steels Nos. 7 (3.5% nickel, 0.7% chromium), 8 (4.5% nickel, 1.25% chromium) and 12 (18% chromium, 8% nickel).

The work described above has been carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research of the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

(f) *THE AQUEOUS IODINE METHOD.*¹

By W. WESTWOOD, B.Sc. (BRITISH CAST IRON RESEARCH ASSOCIATION, ALVECHURCH, BIRMINGHAM).

The revised aqueous iodine method has been operated as described in the Sub-Committee's Third Report.² Results on a representative series of British pig irons are given in Section III.(g) of the present Report. Several of the samples previously reported have been re-examined and revised figures are included. Examination of the results of this investigation shows such small variations between the amounts of individual oxides in different samples, and such a small total-oxygen content, that attention is now being directed to methods yielding a total oxygen figure, aluminium reduction and vacuum fusion, which are likely to be adequate for present purposes.

In order to bring the aqueous iodine method into line with other methods, and to avoid the difficulty of surface oxidation, several attempts have been made to use solid specimens instead of drillings. It was found possible to dissolve the sample completely by prolonging the time of stirring, but there is not yet sufficient evidence to enable any conclusion to be drawn with regard to replacing drillings by solid specimens in the recommended procedure. A little work has also been done on samples taken from various parts of the pig, but any evidence of heterogeneity due to this cause is not yet sufficient for issue.

PART B.—DETERMINATION OF HYDROGEN.

(a) *THE METHODS AVAILABLE FOR THE DETERMINATION OF HYDROGEN IN STEEL.*³

By W. C. NEWELL, PH.D., D.I.C., A.R.C.S., A.I.C. (THE BROWN-FIRTH RESEARCH LABORATORIES, SHEFFIELD).

SYNOPSIS.

A brief review is made of the development of the present-day methods of determining hydrogen in steel. These nearly all involve the vacuum-extraction of the elemental gas at high temperatures either above or below the melting point of the steel. The principles involved in these methods are considered with a view to indicating the probable reliability of the figures obtained by the various methods, as well as to guiding those who may be interested in the setting-up of equipment for the determination of hydrogen in steel. Some notes

¹ Received March 1, 1943.

² *Journal of The Iron and Steel Institute*, 1941, No. I., p. 358 P.

³ Received May 10, 1943.

are added as to the significance of hydrogen in steel, and the various possible systems of expressing the hydrogen content of steel are discussed.

The chief underlying principle of the methods of determining the hydrogen content of steel is the vacuum-extraction of the elemental gas at elevated temperatures. It has been suggested that hydrogen could be estimated indirectly as water after combustion of the metal, and, though Schwartz and Guiler¹ have described a procedure for white cast iron similar to the combustion method for carbon estimation, in which the water formed is swept through and absorbed and weighed in a phosphorus-pentoxide tube, this is not a method which would seem of application to the low hydrogen contents commonly found in commercial steel. Not only is it evident that "wet" chemical methods are not applicable, but it is also a fact that dry conditions have to be maintained during the preparation of the specimens. Such operations as pickling in acid to remove scale are not permissible. When sampling liquid steel for its hydrogen content it is more than ever important that the sampling apparatus should be kept in a rigorously dry condition.

In 1935, Moreau, Chaudron and Portevin² published some results obtained by the ionic bombardment of various metals in the cold, which indicated that the metals contained up to a hundred times as much hydrogen as would normally be obtained by vacuum extraction. Somewhat later Schmid and von Schweinitz³ investigated this method of gas extraction in its application to the determination of the hydrogen content of aluminium sheet. They found that the quantity of hydrogen evolved depended upon the thickness of the sheet, and was roughly proportional to the surface area of the sheet. With thin sheet (down to 0.06 mm.) the hydrogen evolved, calculated on a weight basis on the metal, was certainly high (up to 0.004%), but when comparison was made by vacuum-heating various sheets, similar, and somewhat greater, quantities of hydrogen were evolved, thus suggesting that there had been absorption of water on the surface of the sheet. No further evidence has been forthcoming that ionic bombardment yields figures bearing on the intrinsic hydrogen content of metals.

In view of the ease with which hydrogen diffuses through steel, it would seem to be a matter of importance that hydrogen determinations should be conducted as soon as possible after the receipt of the samples. There is much evidence available (*see*, for example, the conclusions from Section IV.(b) of this Report dealing with the examination of molten steel) that the quantity of hydrogen present

¹ *Transactions of the American Foundrymen's Association*, 1940, vol. 47, p. 742.

² *Comptes Rendus*, 1935, vol. 201, p. 212.

³ *Aluminium*, 1939, vol. 21, p. 772.

in molten or recently cast steel can be much higher than that in steel which has been stored for an extended period. On the other hand, the residual amount of hydrogen found in steel which has been kept for at least a month can be up to 0.0003% for a carbon steel and up to three times this value for an alloy steel, and does not appear to diminish appreciably thereafter. Thus, for steel manufacturing investigations the time interval before the determination of the hydrogen content is made is important, but scarcely so for investigations on steel which has been kept for a long period. The author has observed the evolution in the cold of appreciable amounts of hydrogen from steel shortly after casting, so that it is clearly unsatisfactory to insert a series of such samples into a vacuum-extraction apparatus at any one time.

It has been known for many years that the solution of hydrogen in iron is a reversible process taking place with considerable rapidity at temperatures above 500° C., and much work has been done, not only on the removal of hydrogen by subjecting the metal to a vacuum, but also on saturating the metal with hydrogen at various temperatures and pressures. Determinations of solubility data for hydrogen have been made by Sieverts,¹ as well as by Iwase and Fukisima² and others, whilst many others have confirmed that iron and steel normally contain hydrogen which can be extracted by heating or melting *in vacuo*.

It was observed by Oberhoffer in Germany and by Vacher in America, and later confirmed by Sloman in Britain, that hydrogen was liberated on vacuum-melting steel, and numerous determinations of hydrogen in steel have been made by many workers, including the author, by this method as used for oxygen determinations, since hydrogen is found to be rapidly liberated at the same time. The evolution of hydrogen takes place within the first few minutes of melting, and the amount so extracted is consistent from sample to sample, no further hydrogen being evolved by extending the period of melting *in vacuo*. Further, the more recent work in which steel was melted in the presence of tin for the fractional reduction of the dissolved oxides³ showed that the hydrogen is completely evolved at the lowest temperature employed. Vacuum fusion may, therefore, be looked upon as one of the established methods for the determination of hydrogen in steel, and where the necessary equipment has been installed this is a method confidently used. The Oxygen Sub-Committee as a whole are satisfied that melting *in vacuo*, under the conditions advocated for oxygen determinations, does liberate all the hydrogen present in steel. The

¹ Sieverts, *Zeitschrift für Metallkunde*, 1929, vol. 21, p. 37. See also Sieverts, Zapffe and Moritz, *Zeitschrift für physikalische Chemie*, 1938, A., vol. 183, p. 19.

² *Science Reports of the Tôhoku Imperial University*, 1938, vol. 27, p. 162.

³ Swinden, Stevenson and Speight, Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 321 P.

vacuum-fusion apparatus, however, suffers the disadvantage that very high temperatures of up to $2,000^{\circ}$ C. or more are required for the initial degassing operation, and the technique necessary for dealing with such apparatus as well as the apparatus itself are quite elaborate.

In 1909 and 1911 Baker¹ published two papers upon the evolution of gases from steel at elevated temperatures *in vacuo*, and showed that hydrogen was given off at as low a temperature as 300° C., the rate of evolution reaching a slight maximum at 600° C. Whilst he also showed that hydrogen comprised over 90% of the total gas evolved up to a temperature of 600° C., he also found quite large quantities of carbon monoxide evolved at only moderately higher temperatures. Since Baker encountered large blank errors and apparently found it necessary to extract the gas over periods of time of up to ten days, his results and conclusions should be treated with some reserve.

In 1929 Rooney and Barr,² realising the difficulties of working *in vacuo* and having a problem in which it was probable that the steel samples would contain considerably more hydrogen than usual, put forward a method in which nitrogen was circulated in a closed system over a steel sample heated to 600° C., the hydrogen evolved being estimated from the increase in the thermal conductivity of the circulating gas. They found that the hydrogen evolution was complete in about one hour at 600° C. and detected only a very small amount of a hydrocarbon gas. Since, moreover, these workers found that higher temperatures of up to 900° C. gave no appreciable increase in the amount of gas evolved, it was established that the extraction of hydrogen from steel was complete in a reasonable period of time, a condition which is essential for any practical method for the determination of hydrogen in steel. Somewhat later Inglis and Andrews³ employed this same method, but with the improvement in vacuum technique and equipment most recent workers have preferred vacuum methods, probably because of their greater sensitivity.

Körber and Ploum⁴ used a vacuum-extraction temperature of 400° C., whilst Sloman,⁵ who was responsible for much of the pioneer vacuum-extraction work done in Britain, showed that at 650° C. the evolution of hydrogen normally ceased after 1–2 hr. and that the amount so collected was equal to that collected by vacuum-fusion at 1550° C. The present author,⁶ having examined

¹ *The Iron and Steel Institute, Carnegie Scholarship Memoirs*, 1909, vol. 1, p. 219; 1911, vol. 3, p. 249.

² *Journal of The Iron and Steel Institute*, 1929, No. I., p. 573.

³ *Journal of The Iron and Steel Institute*, 1933, No. II., p. 383.

⁴ *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1932, vol. 14, p. 229.

⁵ Eighth Report on the Heterogeneity of Steel Ingots, p. 43, *The Iron and Steel Institute*, 1939, Special Report No. 25.

⁶ Newell, *Journal of The Iron and Steel Institute*, 1940, No. I., p. 243 P.

the rate of hydrogen evolution from steel over the temperature range of 400–900° C., showed that normally one hour at 600° C. was sufficient for the complete evolution of the hydrogen free from all but traces of other gases, and gave results indicating that for a range of alloy steels vacuum-heating at 600° C. was as satisfactory for hydrogen determination as vacuum-fusion at 1600° C. For this purpose a simple type of glass apparatus was designed and constructed, in which steel samples could be manipulated in and out of a clear-silica-tube furnace by the novel principle of a "mercury lift," by means of which contact between the steel and the furnace wall and any possible interaction were avoided. The advantages of operating under these conditions, as compared with those for vacuum fusion, are that the estimation of the hydrogen is made simply by measurement of its pressure at a definite volume and that the blank is negligible, amounting to only 0.00001 ml. (or 0.000,000,001 g.) per hr., which is only one-hundredth of the corresponding blank obtained under optimum conditions by the vacuum-fusion method.

Since the publication of the paper just referred to, a number of laboratories have installed somewhat similar equipment and for the same purpose. In the following sub-section the author deals with further developments in the apparatus at the Brown-Firth Research Laboratories, whilst in the subsequent two sub-sections accounts are given of experience gained with equipment set up in the Central Research Department of The United Steel Companies, Ltd., and in the Research Department of I.C.I. (Alkali), Ltd. All three laboratories agree as to the value of the method in the investigation of the hydrogen content of steel, and the publication of this Report brings forward extended evidence of its utility and reliability.

Bennek and Klotzbach,¹ in a study of the effect of hydrogen on hair-line crack formation in steel, stated that hydrogen in steel is best estimated by vacuum extraction at 1100° C. in the presence of tin and in a silica tube. This method suffers from the disadvantage that tin is volatilised to cooler parts of the apparatus, where it adsorbs gas which it is difficult to extract completely.

One of the difficulties that one encounters when trying to compare the merits of different methods of determining hydrogen in steel is that there is no certainty that two specimens from the same sample do really contain the same amount of hydrogen. When sectioning ingots the author has found as much as a five-fold variation of hydrogen content between the centre and outside of the ingot, maybe over a distance of only a few inches. The manner in which the specimens are machined from the block of steel is most important. Any appreciable heating of the steel during machining must be avoided, and such operations as sawing and grinding must be performed very slowly. Experience has shown that far too often extraneous variations of hydrogen content

¹ *Stahl und Eisen*, 1941, vol. 61, pp. 597, 624.

between specimen and specimen have probably been introduced during the preparation of the specimens.

As an example of the equivalence of the vacuum-fusion and vacuum-heating methods for the determination of hydrogen in steel, Table XX. shows the collected results on a plain carbon steel, in the ingot form and after various stages of hot-work. The analysis of the cast (No. 52703) was : 0.08% of carbon, 0.07% of silicon, 0.23% of manganese and 0.10% of nickel; further details of the preparation of this cast are given in the Eighth Report on the Heterogeneity of Steel Ingots, p. 204. This steel was cast in November, 1936, but the samples were not distributed until the end of February, 1937, so that several months elapsed during which the hydrogen content of the ingot sample, in particular,

TABLE XX.—*Comparison of Hydrogen Contents Determined in Different Laboratories by the Vacuum-Fusion and Vacuum-Heating Methods upon Cast 52703 before and after Hot-Working.*

Material.	Laboratory.	Vacuum-Fusion Method.	Vacuum-Heating Method.
Ingot.	B.F.R.L.	0.00035	0.000340
	N.P.L.	0.00034	0.000330
	C.R.D.	0.00035	0.000345
	I.C.I.	...	0.000340
		...	0.000350
		...	0.000350
Box test (4 in. square)	B.F.R.L.	0.00015	0.000125
	N.P.L.	0.00007	...
	C.R.D.	0.00010	0.000065
2-in. rolled slab	B.F.R.L.	0.00015	0.000130
	N.P.L.	0.00012	0.000125
	C.R.D.	0.00015	0.000110
$\frac{3}{4}$ -in. rolled bar.	B.F.R.L.	0.00015	0.000110
	N.P.L.	0.00006	0.000080
	C.R.D.	0.00015	0.000050

would have had an opportunity to become stabilised. Vacuum-fusion determinations were made in the various laboratories during 1937 and the beginning of 1938, whilst vacuum-heating determinations were made over the years 1938–1942. Sloman (*loc. cit.*, p. 53) and the present author (*loc. cit.*, p. 247 P) have already published some of the earlier results on this cast, and the significant features about the effect of hot-working upon the hydrogen content have been dealt with. The features to be pointed out here are that there appears to have been no drift or other change in the hydrogen contents over the years 1937–1942, and that the results by vacuum-fusion and vacuum-heating for the ingot sample agree

very well indeed. The figures for the forged samples are lower and show a wider range of variation between the various laboratories and the two methods. These variations are probably real variations in the hydrogen content of the pieces of bar (all cut from one 30-ft. length) distributed to the four laboratories.

The thirteen alloy steels which the Sub-Committee have had for examination were all prepared in the form of rolled $\frac{7}{16}$ -in. rod, and in consequence had many stages of hot-work. These steels were really obtained for examination of their oxygen content by the various methods, but because they were available to all the Members of the Sub-Committee their hydrogen contents have been determined and reported on (*see* Table LXVII. of Section III.(h) below) and call for some comment here. As would be expected after the hot-working that these steels had received, only the two austenitic steels, Nos. 12 and 13, retained much hydrogen at all. With such austenitic steels it is therefore not surprising that vacuum-heating has to be extended for several hours for the complete evolution of all of the hydrogen. The agreement between the results obtained by the two methods (vacuum-melting at 1600° C. and vacuum-heating at 600° C.) and in different laboratories for these two steels is good. In all the other steels in this series the hydrogen contents are only of the order of 0.00005%, which is about the limit of accuracy of the vacuum-fusion method, though, by virtue of the lower blank of the N.P.L. apparatus, the limit of accuracy with this equipment is somewhat better. The figures obtained by the vacuum-heating method are stated to an additional significant figure, because of the greater accuracy of this method in measuring the quantity of hydrogen evolved. The results are in reasonably satisfactory agreement, and even show that the annealing of specimens by one laboratory led to a lower hydrogen result.

Experience with the vacuum-heating method to date has revealed that for steel samples with a hydrogen content of the order of 0.0002% or more, the vacuum-fusion and vacuum-heating methods yield results in close agreement. For steels with a lower hydrogen content the agreement is not so good, the vacuum-fusion results tending to be somewhat higher and not checking up among themselves in different laboratories so well as those obtained by vacuum-heating. It is considered that the reason for this is that the vacuum-fusion results are more subject to error by virtue of the blank correction, and the fact that the hydrogen evolved by vacuum-fusion is mixed with other gases and consequently the accuracy of the hydrogen measurement is less. These conclusions are similar to those of the United States Bureau of Standards.¹

The fact that the apparatus required for the vacuum-heating method is comparatively simple and can be constructed in the

¹ Holm and Thompson, *Journal of Research of the National Bureau of Standards*, 1941, vol. 26, p. 245.

laboratory by a capable glass-blower, together with the facts that the blank is negligible, the accuracy high and the reliability proved over a period of time, would all indicate that this method is the one which in general will be employed for the simple determination of hydrogen in steel.

The Significance of the Hydrogen Content of Steel.

When considering analytical results for the various constituents of steel one is accustomed to looking for the figures for any particular element within a certain numerical range. This range may be determined by such factors as eutectic or eutectoid compositions and limits of solubility, but it is striking that the numerical ranges of content of the various elements in steel are often of widely differing orders of magnitude, and quantities which would be considered as negligible traces for some elements would be of great significance for others. Thus, nickel and chromium are considered in concentrations commensurate with that of the iron also present, 0.1% being about the lower limit of significance. Carbon contents range from about 4% for eutectic cast iron down to 0.01% as the probable lower limit of significance for soft iron. Sulphur and phosphorus have a probable lower significant limit of 0.001%. Coming now to oxygen, the low solubility of oxides and silicates in solid steel leads to their easy visible detection as inclusions in steel if much more than 0.001% of oxygen is present, and the solubility limit in the cold solid metal is probably of the order of 0.0001% of oxygen. On the same line of reasoning, hydrogen, with a solubility in α -iron at 600° C. of only 0.0001%, becomes of interest when concentrations of this magnitude are observed.

The development of the scientific control of steel manufacture over the past fifty years could be briefly summarised as a gradual appreciation of the above and similar facts. There remains much to learn as to the precise influence of alloying elements upon the properties of steel, and that is all the more reason why the concentrations of the alloying elements should be viewed in a proper perspective in relation to their individual chemical and physical properties. Assessing the significance of figures which are further and further beyond the decimal point calls for greater mental effort, but the author is of the opinion that this should be done if any co-ordinated conception of chemical composition is to be retained. Some other system of expression of analytical results, in which the significant range of composition for all the elements is expressed within the same numerical range, might seem desirable, and such a system, taking into account the relative size and weight of the atoms and their chemical affinity, is conceivable, though too revolutionary to be considered seriously now. Percentage composition is probably the best practical mode of expression of analytical results.

Attempts have been made to increase the apparent importance of hydrogen-concentration figures by expressing them in terms of millilitres of hydrogen at N.T.P. per 100 g. of metal, and in other Sections of this Report hydrogen figures have also been so expressed for the benefit of those who are used to this system. It is the opinion of most of the Members of the Sub-Committee that this is an awkward system which has little scientific justification, since volumes of hydrogen at an arbitrary temperature and pressure are related to a weight of steel, but the system has served the purpose of drawing attention to the hydrogen figures. It is also the author's opinion that this system has exaggerated the apparent significance of hydrogen in steel and led to erroneous ideas in this connection. A more rational system would be to use a purely volumetric basis, namely, millilitres of hydrogen at N.T.P. per millilitre of metal. This, however, neglects the great effect of temperature upon the volume of a gas, and still suffers from the disadvantage that the volume of hydrogen when in the free state may have no bearing upon its effect when dissolved in steel. The fact that the amount of hydrogen dissolved in steel at high temperatures, when expressed in terms of volume of free gas, may be many times the volume of the metal does not mean that high pressures of hydrogen exist in the metal. The properties of a substance associated with any particular physical state (solid, liquid or gas) are lost when that substance is dissolved in another substance, and it is only the fact that hydrogen can be so easily removed again in the gaseous state which suggests the contrary idea in this instance.

The factor for converting hydrogen percentages to millilitres per 100 g. is 11,200, and it has been suggested that a smaller and more rational factor of 56 might be used to convert to atomic percentage. However, for complex alloy steels atomic percentage becomes more difficult to use, and is really unjustified for one element where all the others are expressed simply as percentages. Alternatively, some workers have suggested and used the percentage multiplied by 10^4 or 10^5 , a system that has much to commend it, especially when expressing results in tabular or graphical form.

The following shows the equivalence of the systems discussed :

0.0001% of hydrogen.	or 1.12 ml. of hydrogen per 100 g. of steel.
or $1.0 \times 10^{-4}\%$ of hydrogen.	or 0.087 ml. of hydrogen per ml. of steel.
or $10 \times 10^{-5}\%$ of hydrogen.	or 0.0056 atomic-% of hydrogen.

One of the great difficulties in using any other than the simple percentage system is that the terms clash when they are presented side by side with percentage figures for other elements, and in the text it will be found that hydrogen contents have been expressed only as percentages in such circumstances.

(b) *THE VACUUM HEATING METHOD.*(b1) *The Vacuum-Heating Apparatus in Use at the Brown-Firth Research Laboratories.*¹

By W. C. NEWELL, PH.D., D.I.C., A.R.C.S., A.I.C. (THE BROWN-FIRTH RESEARCH LABORATORIES, SHEFFIELD).

(Fig. 2 = Plate XVI.)

SYNOPSIS.

Further developments made at the Brown-Firth Research Laboratories with their apparatus for the heating of steel samples *in vacuo* are reported. Several improvements in design have been made, and the utility of the apparatus has been confirmed.

Since the publication of the description ² of the apparatus which the author designed especially for the manipulation of steel samples *in vacuo*, for the extraction of their hydrogen content at only moderately elevated temperatures, the apparatus has been improved (see Fig. 2).

Operating at a temperature of only 600° C. instead of the temperatures of up to 1000° C. which were employed in the preliminary work, it was found that the radiation and conduction of heat from the silica furnace tube was so moderate that it was possible to reduce the length of furnace tube by several inches. As a safeguard against overheating of the grease on the joint between the furnace tube and the Pyrex tube beneath, black Apiezon wax *W* is used on this joint in place of grease; in this way the red-hot samples can be brought down straight from the furnace to the sample-tube level without any fear of gas being evolved from the joint. Moreover, it is our practice in the early stages of out-gassing a new apparatus to bring down a red-hot sample into the Pyrex tube repeatedly to bake out this part of the apparatus.

Another decided improvement is that the spacing of the side tubes has been so arranged that there is only one lower position for the platform, and this position is used both to deliver the samples on to the platform and to remove them from it. The position is determined by a support which prevents the further downward motion of the platform, so that the lower position of the latter has not to be carefully adjusted, as was the case earlier, and all that is necessary is a restriction in the connecting tubing which automatically checks the rate of movement of the platform. With full atmospheric pressure on the lower mercury surface, the platform rises to its maximum height, when it is then in the correct position

¹ Received March 12, 1943.

² Newell, *Journal of The Iron and Steel Institute*, 1940, No. I., p. 243 P.

in the furnace. By a turn of the two-way tap the lower mercury surface can be exposed to a rough vacuum when the platform descends to its lower position, the whole mercury-float and connecting rod being suspended from the support under the platform in this position. The means whereby only one lower position is now required is obtained by the attachment of the two sample tubes to the main vertical tube, the one $\frac{1}{4}$ in. above and the other $\frac{1}{4}$ in. below the fixed platform level. In this way the fresh samples can be magnetically dropped upon the platform, and the heated samples can be magnetically pushed off the platform and dropped into the receiving sample tube. This leads to an arrangement of four side tubes spaced close together and sealed radially at 90° into the main vertical Pyrex-glass tube. This also reduces the length of the main vertical tube by a few more inches, so that with this and the shortening of the furnace tube the height of the apparatus is substantially less, and is now only 50 in. The apparatus is now housed in a suitable wooden box, which stands on the bench, so that the controls of the apparatus are all at a very convenient manipulating level.

Much consideration was given as to a suitable supporting collar for the platform at its lower position. The collar had to be of such a form that it could be placed in position after the intricate glass-blowing operations, and it then had to be fixed centrally in that position. Numerous attempts were made with glass and bakelite collars fixed by wax, but these were either too tight in the glass tube or else moved out of alignment owing to softening of the wax. The method now employed is very simple and free from any objections. A length of thin-gauge cold-rolled stainless-steel strip, about 3 cm. wide, is first rolled up into a tight spiral or spring and then pushed into the glass tube, where it grips by the action of the expanding spiral and leaves at its centre a cylindrical space through which the stainless-steel tube supporting the platform can be passed. Such a supporting system not only resists the action of the hot platform but is easily adjusted and removed when necessary. Moreover, it also guides the stainless-steel tube when the platform is being raised or lowered, so that the platform is kept centralised in the tube.

The magnet used earlier for moving the samples was a straight mild-steel electro-magnet. This was rather heavy and the attached electric flex was sometimes inconvenient, so that we tried using permanent magnets. Thanks to the courtesy of Messrs. Swift Levick, we are now fitted up with permanent magnets of high coercivity, and which are of such a shape that the two poles just span the various tubes of the apparatus. One of the magnets is of the type used for moving-coil electrical meters, and has a hollow pole-piece which just fits over and normally hangs on one of the glass tubes. This is used for moving the ram to remove samples from the platform, and can be seen in the front of the photograph of the apparatus (Fig. 2).



FIG. 2.—The Vacuum-Heating Apparatus for Determining Hydrogen in Use at the Brown-Firth Research Laboratories.

[Fourth Report of the Oxygen Sub-Committee.
[Section II., Part B (b1).
[To face p. 288 F.



FIG. 3.—Apparatus for the Vacuum-Heating Method of Determining Hydrogen Used at Stocksbridge.

*[Fourth Report of the Oxygen Sub-Committee.
[Section II., Part B (b2).
[To face p. 289 p.]*

The mercury-vapour pump is made of Pyrex glass and has two stages, the first being for high-speed low-pressure pumping-away of the hydrogen and the second being of the high-pressure type, capable of withstanding a pressure of a few millimetres of mercury. Such a pump can hold back all the hydrogen that we have encountered from any steel sample without the need of action with the Töpler pump during the course of the determination. The boiler of the mercury pump is of cylindrical design with the return tube for the liquid mercury connecting in the lower central position of the boiler. With this design electrical heating is simpler to apply with a very steady boil. The boiler is about 5 cm. high and is completely wound with Nichrome resistance tape, whilst the depth of mercury is only about 1 cm. In addition, the resistance tape is wound with a wider spacing between turns right the way up the rising vapour tube. In this manner quite a considerable amount of heat must be transmitted to the mercury by radiation from the upper part of the heated boiler, and the condensation of mercury in the rising vapour tube is eliminated. This avoids any excessive heating of any part of the pump and leads to very steady pumping. The capacity of the Töpler pump is about 300 ml., and the capacities of the three bulbs used for measuring the hydrogen are, in ascending order, 8 ml., 2 ml. and 0.3 ml. The volume of the system between the mercury-vapour pump and the Töpler pump has been reduced still further, and can now be only about 25 ml., as thirteen-fourteenths of the total gas is collected in the first sweep of the Töpler pump.

It has been found that, once the apparatus has been thoroughly baked out under a good vacuum, air can be admitted and fresh samples inserted into the apparatus, which can then be re-evacuated with a total delay of only about a quarter of an hour. This means that additional samples can be examined in the apparatus and a figure for the hydrogen content obtained in somewhat over an hour. This shows that there is no important absorption of gas within the apparatus when it is exposed to air for a short period, and is a very pleasing feature when compared with the corresponding delay entailed under such conditions with the vacuum-fusion apparatus. In consequence it is not necessary to insert as many samples in the sample tube as was our custom—certainly not more than can be dealt with in a day, *i.e.*, 6–8 samples. It is for this reason that the two sampling tubes are now only about 6 in. long.

The two glass bottles which were used as reservoirs for the mercury have been replaced by bulbs of such a shape that a minimum of excess mercury is used in the apparatus. The narrow tube attached to the base of the bulb containing the mercury for the mercury lift is incorporated, so that variations in the barometric pressure chiefly affect the level of the mercury in this tube in preference to the upper mercury level on which the platform is floating.

On the whole, therefore, decided improvements have been incorporated in the apparatus, which have led to still greater simplifications and ease of operation.

The results obtained continue to be instructive and to agree reasonably well with those produced by the vacuum-fusion method, as shown in Table LXVII., giving the results for the thirteen alloy steels.

The author wishes to express his thanks to the Directors of Messrs. Thos. Firth and John Brown, Ltd., and Messrs. Firth-Vickers Stainless Steels Co., Ltd., for their agreement to publish details of the apparatus, and especially to Dr. W. H. Hatfield, F.R.S., for encouragement during the various stages of its development.

(b2) *The Vacuum-Heating Apparatus at the Central Research Department, The United Steel Companies, Ltd., Stocksbridge.*¹

By W. W. STEVENSON, A.I.C., AND G. E. SPEIGHT, B.Sc., A.I.C.
(Under the direction of T. Swinden, D.Met., Director of Research.)

(Fig. 3 — Plate XVII.)

SYNOPSIS.

A description is given of the apparatus and method of operation for the vacuum-heating or low-temperature extraction method for the determination of hydrogen in steel. A few typical results obtained are also included.

The apparatus at the Central Research Department has been based on that described by Newell and incorporates the mercury lift. Other features have been added, including a delivery tube to the modified McLeod gauge, whereby gas samples, after being measured in the McLeod, can be collected in a gas sample tube by the action of the Töpler pump. The major difference, however, is the addition of a very large tap and secondary evacuation circuit, such as that described by Willems,² the purpose of which is to permit the introduction of samples to the apparatus while still maintaining the vacuum in the other parts of the equipment, including the mercury lift and heating furnace. Willems described several forms of taps and other devices, whereby steel specimens could be passed from an outer to an inner sample tube. The simplest of these arrangements is the wide-bore tap, the ends of the bore being radiused, so that in the open position of the key the surplus grease is

¹ A communication from the Central Research Department, The United Steel Companies, Ltd., Stocksbridge, near Sheffield, received March 12, 1943.

² Willems, *Archiv für das Eisenhüttenwesen*, 1938, vol. 11, p. 627.

taken up by a trough between the key and barrel, thus enabling specimens to be passed without contamination by the grease lubricant.

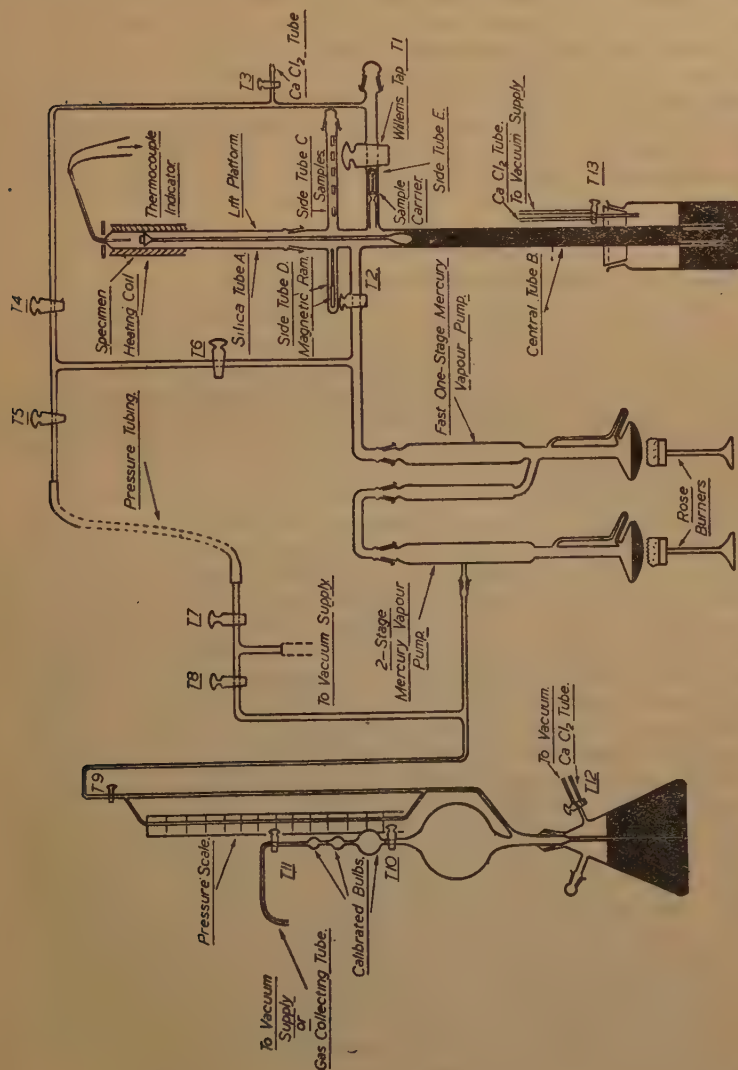


FIG. 4.—Apparatus for the Vacuum-Heating Method of Determining Hydrogen in Use at Stocksbridge.

The wide-bore tap, used in the manner described by Willems, has not proved entirely satisfactory, owing to its grease trough being inadequate to take up the surplus amount of lubricant necessary

for this large tap. The objection has been overcome by the use of a small "carrier," illustrated in Fig. 4, which consists of a short length of glass tube, one end of which is open and the other closed after sealing inside a small length of soft iron. The external diameter of the glass carrier just passes through the bore of the Willems tap and the internal diameter is sufficiently large to hold a steel specimen 10–11 mm. in dia. Thus, by operating on the soft iron with a hand magnet from outside, the carrier can be moved bodily through the tap and the specimen so transferred from the outer to the inner vacuum chambers. Contamination of the specimen by the lubricant of the Willems tap is thereby obviated.

Description of the Apparatus.

(a) The Main Circuit, Excluding the Willems Tap.

A detailed description of the apparatus, illustrated in the photographs, Fig. 3, and outlined in the diagrammatic sketch, Fig. 4, is as follows: The furnace tube *A* is of transparent silica, 16 in. in length and $1\frac{3}{8}$ in. in internal diameter, and round the upper 6 in. is wound a nickel-chromium resistance wire, well insulated by several layers of asbestos cord. The upper end of the tube is reduced and sealed to a 6-in. length of $\frac{3}{8}$ -in. silica tube, which is bent at an angle of 60° to the tube *A* and through which a thermocouple (connected to a temperature recorder) is inserted and sealed with vacuum wax, so that the hot junction of the couple projects about 3 in. down the centre of the main silica tube (*A*). The lower end of the silica tube terminates in a ground joint, which fits a corresponding taper on a Pyrex tube *B*, 36 in. in length, carrying side arms for the sample chambers and mercury-vapour pumps. The lower open end of tube *B* passes below a mercury surface and almost reaches the bottom of the containing bottle, the opening to which is closed by an india-rubber bung, carrying a three-way tap which connects to atmospheric pressure and vacuum supply, respectively. Floating vertically on the mercury surface inside the tube *B* is a transparent silica tube, 28 in. in length, closed at the lower end by a hollow bulb, acting as float, and terminating at the top in a flat platform with conical sides. The diameter of the platform is approximately $\frac{1}{10}$ in. smaller than the internal diameter of the tubes *A* and *B*. By turning the three-way tap to the vacuum supply, the platform may be lowered to the level of the side tubes to receive or discharge a specimen, and by opening to atmosphere the platform and specimen may be raised to a predetermined position in the furnace tube *A*. Whilst this arrangement can be seen clearly in the sketch, Fig. 4, it is not apparent in the photographs, Fig. 3, because the lower portions of tube *B* and the mercury reservoir are below the bench level.

The two upper side tubes *D* and *C* attached to the central glass column *B* are for the purpose of removing and storing specimens

after testing. In the smaller tube, *D*, is placed a light pusher consisting of a short length of soft iron attached to a 3-in. length of glass tubing. Thus, on being activated by an external magnet, the push-rod forces the degassed specimen from the platform into the opposite and larger tube (*C*). The tube *C* is capable of storing 10–12 specimens and is fitted with a ground joint and cap to facilitate withdrawal of the specimens from the apparatus. The two lower side tubes *E* and *F* are connected to the central column at right angles, tube *F* serving as the outlet for the gas to the mercury-vapour pumps, whilst tube *E*, which carries the Willems tap T_1 , is the inlet and storage chamber for new specimens prior to testing. Connecting these two side tubes is a secondary circuit leading to the mercury-vapour and oil pumps; this circuit will be described later in connection with the operation of the Willems tap.

The mercury-vapour diffusion pumps consist of a one-stage wide-bore unit, followed by a standard double-stage pump, the combined assembly being designed for speedy and efficient collection of the evolved gas. Both units are in heat-resisting glass and are gas-heated.

The outlet of the standard mercury-vapour pump leads directly to a combined McLeod gauge and Töpler pump, used primarily to collect and measure the quantity of evolved gas and secondly to transfer this gas after measurement to a gas-sampling tube and thence to an Ambler gas-analysis apparatus. This unit comprises a large bulb of 400-ml. capacity joined to three successively smaller bulbs of 16-ml., 3-ml., and 0.7-ml. capacity, the three smaller bulbs being isolated from the remainder of this unit by two taps, T_{10} and T_{11} . The McLeod gauge is operated by the two-way tap T_{12} , which opens either to atmosphere or to the vacuum supply. The quantity of gas evolved from a specimen is measured by compression until its volume enclosed below T_{10} corresponds to one or other of the calibrated marks. The pressure of this known volume of gas is noted on the scale on the outer tube of the McLeod gauge and the volume at N.T.P. obtained by direct calculation. This McLeod gauge is extended into the Töpler pump by the vertical capillary tube connected above the upper tap T_{11} leading to a gas-sampling tube at the outlet end. Thus, after pressure measurement, the evolved gas may be transferred to a sampling tube filled with mercury.

Inserted between the mercury-vapour pump and the McLeod gauge is a branch tube leading to the vacuum supply—a mechanical one-stage oil pump. This latter serves as the backing pump for the vapour pumps during the initial evacuation of the apparatus, and is also used as the vacuum supply for the other parts of the apparatus—the McLeod gauge and the central column of the mercury lift in tubes *A* and *B*.

(b) *The Secondary Circuit and Willems Tap.*

As mentioned before, the two lower side tubes *E* and *F* are connected by a secondary circuit whereby a separate chamber, isolated from the main circuit, can be evacuated by the oil pump and finally by the mercury-vapour pumps. The special Willems tap T_1 is situated at the mid-point of side tube *E*, and from a point between this tap and the ground joint closing the side tube this circuit leads to the other side tube *F* midway between tap T_2 and the first mercury-vapour pump. Outlets to the oil pump and to atmosphere are provided for this circuit, and each section may be isolated separately by the taps T_4 , T_5 and T_6 .

The introduction of metal samples to the apparatus is achieved as follows: On opening tap T_3 cautiously, dried air is admitted and atmospheric pressure restored to the outer chamber between T_1 and T_4 . After removing the ground cap on tube *E* the sample carrier charged with a specimen is inserted and the cap replaced. Evacuation of the outer chamber is obtained initially by the oil pump via T_4 and T_5 and completed by the mercury-vapour pumps through tap T_6 , after isolating the oil pump by T_5 . Tap T_1 is opened and the specimen carrier passed through by means of the external magnet. Finally, the specimen is transferred to the platform and hence to the furnace, and after withdrawing the sample carrier tap T_1 is closed, tap T_2 opened and the outgassing of the apparatus completed. In this manner specimens may be introduced into the apparatus when it is necessary to complete individual determinations in a limited time, thereby avoiding the delay due to cooling, admitting air and recharging in the usual manner. The apparatus may also, of course, be used in the more usual fashion by initially charging a number of specimens, since the side arm is capable of holding 10–12 specimens each of approximately 15 g. weight.

Procedure for the Determination of Hydrogen in Steel.

The experimental procedure for the determination of hydrogen is as follows: Cylindrical specimens of 20 mm. length and 10 mm. dia., after careful machining, avoiding overheating and grease contamination, are cleaned in carbon tetrachloride and weighed. The usual determination requires one such piece weighing 13–14 g. Tap T_3 and the ground joints on tubes *E* and *C* are closed, the specimen platform resting at its normal position below side tube *E*. The vacuum supply is applied to the apparatus, and at the same time the mercury levels in the McLeod gauge and the central column *B* are maintained at their normal positions. Taps T_5 and T_7 are closed, the mercury-vapour pumps are heated and the furnace is switched-on. After approximately 20 min. the furnace attains 600° C., and the specimen platform is gradually elevated to

its predetermined position in the centre of the furnace by opening tap T_{13} to atmosphere. The sample platform is heated for 60 min. and then slowly lowered past the ground joint between tubes A and B , being arrested at the level of side tube E . Owing to the very slow cooling of the platform under vacuum, this operation must be carried out very cautiously to avoid overheating the grease joint, which would cause gas evolution from the grease. A current of cold air directed on this joint assists materially in this object. After closing taps T_1 and T_4 the first specimen is admitted to the outer chamber, which is then re-evacuated by the oil and diffusion pumps, as previously described. After passing the specimen into the main apparatus the sample carrier is withdrawn, the oil pump isolated by tap T_8 and the residual gas swept from the apparatus through tap T_{11} . Tap T_{11} is closed and the mercury level in the McLeod gauge lowered to its normal position. The small quantity of gas remaining in the apparatus is then measured in the McLeod gauge, although the difference in mercury levels at this stage is usually nil prior to the extraction of hydrogen.

The specimen is now raised on the platform lift into the heated part of the furnace, and on attaining 600° C. rapidly evolves gas, which accumulates in the large bulb of the McLeod gauge. The course of the gas evolution may be followed by periodic compression into the smaller bulbs, noting the pressure of the gas when its volume equals one or other of the calibrated volumes. The quantity of gas so collected at this stage is confined in the smaller bulbs by tap T_{10} , leaving the large bulb free for the further collection of gas. By taking observations in this manner it is seen that a very rapid evolution of gas occurs in the initial stages, but after about 25–30 min. the rate of evolution decreases to a very small value corresponding to the blank in the apparatus. It is usual to allow at least 60 min. for the heating and complete degasification of the specimen. At the end of this period, final pressure readings are obtained, and if it is desired to make an analysis the gas sample is swept into a small sample tube. If analysis is not required, the gas is swept out of the apparatus by the oil pump. Meanwhile, the platform and degassed specimen are lowered slowly until the platform reaches the storage tube C , into which the specimen is transferred by the magnetic ram in side tube D . Cooling of the platform and specimen is even slower than that of the platform alone, and it is usual to allow about 25–30 min. for the complete change. The apparatus is now ready for the next specimen, which is admitted into the outer chamber during the degasification of the previous sample.

Results Obtained.

A selection of typical hydrogen contents determined by the foregoing technique on a variety of materials is given in Table XXI., together with corresponding results by the vacuum-fusion method,

where available. Fig. 5 shows the progress of the gas evolution during the vacuum-heating at 620° C. of a number of samples from the same cast of steel.

TABLE XXI.—*Typical Hydrogen Results by the Vacuum-Heating Method.*

Sample.	Hydrogen Content.			
	Vacuum-Fusion Method.		Vacuum-Heating Method.	
	%.	Ml. per 100 g.	%.	Ml. per 100 g.
<i>Cast H621. 5% Nickel Steel, Basic Electric Arc.</i>				
Furnace "test bit" at "melted." Carbon 0.69%	0.00020	2.0	0.000150	1.65
Furnace "test bit" during refining. Carbon 0.10%	0.00020	2.5	0.000215	2.40
Furnace "test bit" prior to tapping. Carbon 0.11%	0.000305	3.40
Pit sample (1½ in. square)	0.00015	1.5	0.000095	1.05
Billet (3½ in. square): Centre	0.000250	2.80
Outside	0.000115	1.30
Forged bar (1½ in. dia.)	0.000045	0.50
Forged bar (¾ in. dia.)	0.00005	0.5	0.000060	0.65
<i>Cast H624. 5% Nickel Steel, Basic Electric Arc.</i>				
Furnace "test bit" at "melted." Carbon 0.70%	0.00025	3.0	0.000215	2.40
Furnace "test bit" during refining. Carbon 0.09%	0.00025	3.0	0.000320	3.55
Furnace "test bit" prior to tapping. Carbon 0.13%	0.00025	3.0	0.000255	2.85
Pit sample (1½ in. square)	0.00020	2.0	0.000140	1.55
Billet (3½ in. square): Centre	0.000195	2.15
Outside	0.000120	1.35
Forged bar (¾ in. dia.)	0.00010	1.0	0.000065	0.70
<i>Cast 3341. 1% Chromium-Molybdenum Steel, Basic Electric Arc.</i>				
Furnace "test bit" prior to tapping. Carbon 0.29%	1	...	0.000160	1.80
	2	...	0.000170	1.90
	3	...	0.000155	1.75
	1	...	0.000165	1.85
	2	...	0.000135	1.50
Pit sample (2 in. square). Six determinations on same sample	3	...	0.000130	1.45
	4	...	0.000105	1.15
	5	...	0.000105	1.15
	6	...	0.000160	1.85

Comments on the Results in Table XXI.

(1) The graphs in Fig. 5 indicate that the rate of evolution of gas at 600° C. is exceedingly rapid, more than 90% being collected in the first 30 min., including an appreciable time interval for the transfer of the specimen to the furnace and attainment of temperature. In the majority of steels gas collection for 60 min. suffices to recover the full hydrogen content, so that very little improvement is to be expected by increasing the temperature of evolution.

However, it was found that with austenitic steels the gas evolution at 600° C. is substantially slower than with ferritic steels, and, whilst temperatures up to 850° C. yielded an improvement, the rate of evolution was still much inferior to that of ferritic steels at 600° C. This phenomenon is associated with the structure and permeability of the iron lattice, which allows easier diffusion of hydrogen in the α than in the γ form.

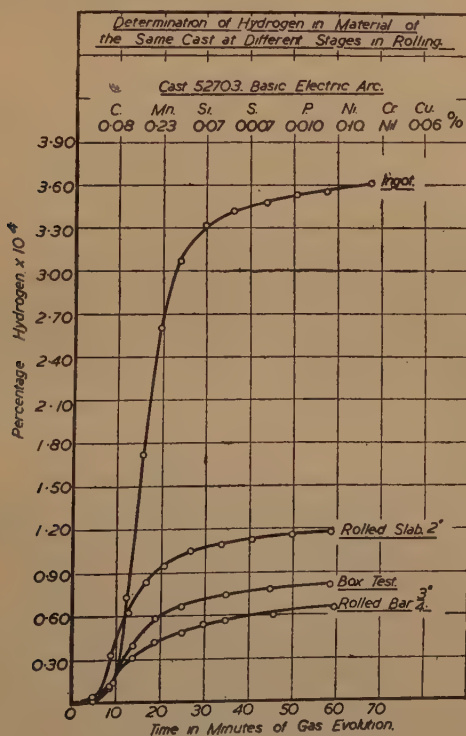


FIG. 5.—Progress of Gas Evolution at 620° C.

(2) The results in Table XXI. illustrate the accepted accuracy of the two hydrogen techniques as practised in these laboratories and the extent of agreement between the two procedures. There appears to be a slight tendency towards a lower result with the vacuum-heating method, but this is undoubtedly connected with the precise evaluation of the blank in the vacuum fusion process.

(3) The great variability of the hydrogen contents of small cast-steel specimens is shown by the result for cast 3341, where six samples cut from one "test bit" give results ranging between 0.000105% and 0.000165% of hydrogen.

(b3) *Apparatus Used at I.C.I. (Alkali), Ltd., for the Determination of Hydrogen by the Vacuum-Heating Method.*¹

By E. W. COLBECK, M.A., AND S. W. CRAVEN, A.M.C.T. (NORTHWICH).

SYNOPSIS.

A description is given of an apparatus for the determination of hydrogen by the vacuum-heating method, embodying the use of magnetic control for the movement of specimens. The method of operation is described.

When the determination of hydrogen by the vacuum-heating method at I.C.I. (Alkali), Ltd., was first considered, it was decided to erect an apparatus similar to that described by Newell,² in which the steel sample is heated in a high vacuum at a temperature of 600° C., a mercury lift being employed to move the samples vertically in and out of the furnace. Several manipulative difficulties were encountered with the apparatus built at Winnington :

(1) The transfer of the specimens from the side-arm to the mercury lift was a little uncertain; it is important that the test-piece should occupy a central position on the platform, thus helping to ensure that the lift moves vertically upwards without a tendency to knock against the sides of the glass guiding tube or the silica furnace tube. Prevention of this lateral movement is particularly necessary at the point where the specimen and platform pass the greased joint connecting the furnace tube to the main body of the apparatus, because of the danger of the pick-up of grease which would subsequently "crack" on heating at 600° C.

(2) Obtaining a constant blank of a sufficiently low order was a tedious operation. The large volume of mercury employed is capable of retaining considerable quantities of air and/or water vapour. In Newell's apparatus it was not possible to expose the mercury or the Töpler-McLeod portion of the system to the very high vacuum produced by the mercury-vapour pump to facilitate their complete degassing.

It was therefore decided to modify the existing apparatus as shown diagrammatically in Fig. 6. The mercury-lift principle has been abandoned in favour of simple magnetic control; the handling of magnetic specimens is very easy and the movement of non-magnetic specimens by means of a magnetic "pusher" is quite satisfactory. The movement of non-magnetic specimens is very much facilitated if care is taken to keep the underside of the silica tube perfectly level and to avoid any bulging at the junction

¹ Received March 12, 1943.

² *Journal of The Iron and Steel Institute*, 1940, No. I., p. 243 P.

of the two side-arms. The other modifications consist essentially in connecting the outer end of the McLeod gauge to the three-stage mercury-vapour pump and inserting a second single-stage mercury-vapour pump in the leg of the tube connecting the delivery end of the three-stage pump to the Töpler pump. This enables the whole of the McLeod-Töpler unit up to the tap *H* to be evacuated by means of the three-stage mercury-vapour pump, while the length of tube between tap *H* and the delivery end of this pump is exhausted by the second single-stage pump. Arrangements were also made for an easy and rapid restoration of the whole system to atmospheric pressure.

The apparatus shown in Fig. 6 is not the simplest arrangement, and it would be possible to reduce the number of taps if an entirely new apparatus were constructed.

The Apparatus.

The whole apparatus, except for the furnace tube and side-arms, was constructed from Pyrex glass, the mercury-vapour pumps, the Töpler pump and the McLeod gauge being sealed on in position. The furnace tube was made from transparent silica tubing. The volumes of the bulbs *x*, *y* and *z* of the McLeod gauge were determined experimentally before the erection of the apparatus.

All taps and joints were greased with Apiezon grease *M*.

Method of Operation.

The apparatus is assembled as shown in the diagram, the cleaned and weighed specimens being in one of the side-arms. Taps *C*, *D*, *E*, *F*, *H*, *J* and *K* are opened; tap *A* is closed. Taps *B* and *G* are then opened to vacuum, and with tap *I* closed the Hyvac pump is started up and the buffer system between it and tap *I* evacuated. Tap *I* is then slowly opened to the system, and pumping is continued until most of the air has been evacuated from the apparatus. The two mercury-vapour pumps are then started up, and taps *B*, *C*, *G* and *H* are closed. The furnace is brought up into the position shown in Fig. 6, switched on and its temperature raised to 600–650° C. The outgassing process is continued, preferably overnight. Taps *I*, *J*, *K*, *D* and *E* are then closed and tap *H* is opened. After tap *A* has been opened, tap *G* is also opened cautiously to admit air into the top of the mercury reservoir and so to force the mercury upwards into the second large bulb of the Töpler-McLeod unit and thence into the calibrated bulbs. The mercury level is carefully adjusted to the higher calibration mark *z*, and the difference in height between this mercury column and that in the adjacent tube is read off on the scale *S*. Any difference in height between the two mercury columns at this stage indicates a leak in the apparatus or incomplete evacuation. In the absence of any difference in level, the mercury is brought back into the bottom reservoir of the Töpler-McLeod

unit by opening tap *I* to the Hyvac pump and drawing the air from the reservoir by opening tap *G* to vacuum. Taps *I* and *G* are then closed again and a blank on the apparatus is determined by collecting

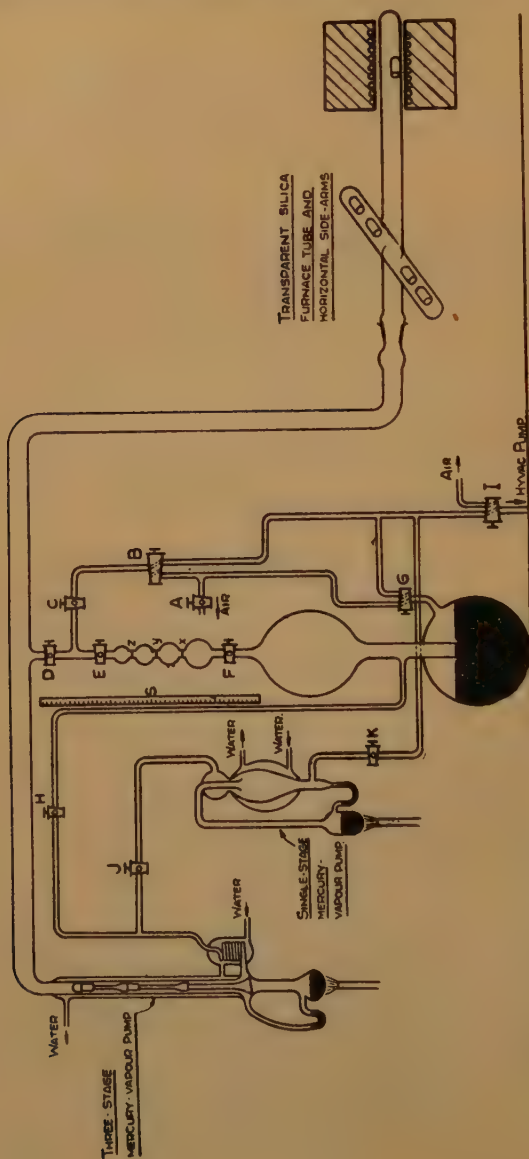


Fig. 6.—Vacuum-Heating Apparatus for the Determination of Hydrogen in Use at Winnington.

the gas delivered by the three-stage mercury-vapour pump in one hour and measuring its volume and pressure in the manner outlined above. In practice, this blank never exceeds 0.0005 ml. per hr. and is generally much smaller than this maximum figure.

If the blank figure is satisfactory the determination of hydrogen in a steel sample can follow. The furnace is drawn back to expose the full length of the furnace tube, and the specimen is brought up to a predetermined mark by magnetic means (using a magnetic pusher from which the hydrogen has been previously removed, if the sample is non-magnetic). After this the furnace is brought back to the position indicated in Fig. 6. The gas evolved in a given time is then collected and compressed into the calibrated bulbs, and its volume and pressure are noted. The procedure suggested by Newell (*loc. cit.*) of taking only one sweep of the Töpler pump and using an experimentally determined factor to convert the quantity of gas measured to the total volume of gas evolved is followed. With the apparatus used by the authors one sweep of the pump collects about nine-tenths of the gas actually present. Heating of the specimen is continued until the evolution of gas ceases, and it should be noted here that the curves shown by Newell indicating the relationship between the hydrogen evolved from steel and the time at various temperatures has been confirmed by the present authors.

The apparatus is brought back to atmospheric pressure in the following way: At the conclusion of a series of tests, the mercury is brought into the lower reservoir of the Töpler pump, taps *G* and *I* are closed, taps *J* and *K* are opened, and the burners beneath the mercury-vapour pumps are turned off. Taps *D* and *E* are closed and taps *A*, *B* and *C* opened to admit a small volume of air, after which tap *A* is again closed. After cautiously opening tap *G*, so causing a slight rise in the mercury towards the second large bulb of the Töpler-McLeod unit, and then balancing this by opening tap *D* a little, taps *D*, *G* and *E* can be fully opened and the inlet of air controlled by manipulating tap *A*.

The authors wish to acknowledge their indebtedness to Mr. H. J. Welbergen, of the Research Department, I.C.I. (Alkali), Ltd., who was responsible for the erection of the vacuum-heating apparatus, and to Mr. J. B. Cotton, also of the Research Department, I.C.I. (Alkali), Ltd., for his helpful suggestions concerning modifications to the apparatus and assistance in its calibration.

PART C.—DETERMINATION OF NITROGEN.

(a) *GENERAL STATEMENT ON METHODS AVAILABLE.*¹

By T. SWINDEN, D.MET. (CHAIRMAN OF THE SUB-COMMITTEE).

SYNOPSIS.

A general account is given of the principal methods used for the determination of nitrogen in steel.

The determination of the small but definite quantities of nitrogen normally found in iron and steel and the modification of the properties of ferrous materials as a consequence of this associated nitrogen have claimed the interest of metallurgists for a considerable part of the last hundred years. The literature on the subject is very voluminous and beyond the scope of this brief note, but an excellent bibliography up to 1935, compiled by G. C. Lloyd, is available.²

The vacuum fusion method, as applied to the determination of oxygen in steel, is one of the many procedures which have been recommended in the past for the determination of nitrogen. This method has been described in detail in several of the Sub-Committee's Reports.³ It was observed, at an early stage of the work, that not only did the gaseous products of this reduction contain carbon monoxide and hydrogen, but, in addition, nitrogen in quantities equal to those normally found in many types of steel by other methods. Several individual Members of the Sub-Committee have subjected this method to critical examination from this aspect during the course of several years, and consequently, although the original terms of reference of this Sub-Committee were related only to the determination of oxygen, perusal of the Sub-Committee's Reports will reveal many references to the determination of nitrogen. The work covered by the present Report has been concerned to a great extent with this subject, and, moreover, in view of the present enhanced interest in the effect of nitrogen in steel, it has been considered advisable by the Sub-Committee to state the present position of the determination of this element by the more commonly known methods.

The methods of analysis hitherto employed may be divided into two main groups :

(1) Methods in which the nitrogen is liberated as the gaseous element.

¹ Received January 22, 1943.

² Sixth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1935, *Special Report No. 9*, Section VII., p. 121.

³ First, Second and Third Reports of the Oxygen Sub-Committee, *Iron and Steel Institute*, 1937 and 1939, *Special Reports Nos. 16* (Section IV.) and 25 (Section VI.); *Journal of The Iron and Steel Institute*, 1941, No. I., p. 295 p.

(2) Methods in which the nitrogen after conversion into ammonia is measured by accepted analytical methods.

The most important member of the first group, practised at the present time, is the vacuum fusion method of melting the sample in a graphite crucible in a vacuum, whereby the resulting gases are collected and analysed by the conventional methods. As mentioned earlier, previous work of the Sub-Committee has amply confirmed the accuracy and wide applicability of this technique to the determination of nitrogen in steel, even in the presence of the more stable nitrides such as chromium, titanium and vanadium.

The most common method of the second group, in which the nitrogen constituent of the steel is converted to ammonia and subsequently measured by conventional chemical methods, consists of solution of the sample in mineral acid, followed by distillation of the ammonia from alkaline solution. If the nitrides present are completely soluble in the acid, the method offers little difficulty, but the voluminous literature of the last sixty years would suggest that such is not always the case. In fact, much of this work has dealt with the necessity for obtaining complete decomposition of the nitrides, or nitrogen-bearing compounds, by modification of the original solvent.

It is hoped, therefore, that the following sub-sections, which put forward the experience of the Sub-Committee with these methods, will be of assistance in clarifying many of the diverse statements previously made concerning the determination of nitrogen in ferrous materials.

(b) *THE VACUUM FUSION METHOD.*¹

BY T. SWINDEN, D.MET. (CHAIRMAN OF THE SUB-COMMITTEE).

SYNOPSIS.

Observations are made on the vacuum fusion method for the determination of nitrogen in iron and steel. The general applicability and possible sources of inaccuracy of this method are discussed.

The vacuum fusion process for the determination of oxygen in steel has been described very comprehensively in the previous Reports of the Sub-Committee² and many references to the simultaneous determination of nitrogen are made therein. The extension of this method to the determination of nitrogen (and hydrogen) necessitates only a complete analysis of the gaseous products of the reduction, a practice which has, of course, been generally adopted by the Sub-Committee.

¹ Received January 22, 1943.

² First, Second and Third Reports of the Oxygen Sub-Committee, *loc. cit.*

It is recognised that the chemical method determines the nitrogen present as nitrides but not that possibly present in the "free" or gaseous state, whilst the vacuum fusion method should determine the total nitrogen present. Since the evidence available strongly suggests that the free or gaseous mode of occurrence, if at all possible, is too small to permit of its measurement, comparison between the chemical and vacuum fusion methods forms a convenient method of checking results by the latter method. The examples quoted by Stevenson and Speight on p. 81 of the Seventh Ingots Report and by Sloman on p. 48 of the Eighth Ingots Report are typical of the good agreement observed between the two methods, particularly with carbon steels. Although it has been suggested that equally good agreement may not be obtained with alloy steels, results obtained over a number of years in the author's laboratory are, in the main, satisfactory.

Whilst it has also been the experience of the Sub-Committee that similar close agreement between the two methods is almost the invariable rule, exceptional cases have been recorded :

(a) When the vacuum fusion method shows a higher result than the normal chemical method. This occurrence is not due to the presence of "free" or gaseous nitrogen, but has been traced to the incomplete decomposition of stable nitrides of certain elements such as titanium (and possibly molybdenum) by the usual solvents. This phenomenon will be discussed more fully in the following sub-section.

(b) When the vacuum fusion method gives a lower result than the chemical method.

Occasional cases have occurred in which the vacuum fusion method gave the lower result, the difference being rather greater than can be accepted as a normal experimental difference. Inspection of many results suggests that although agreement is close and well within experimental limits, there exists a slight but general tendency for the vacuum fusion method to yield the lower result. This has been noticed by other collaborators, and attention to its occurrence in certain alloy steels was directed by Sloman in the last Sub-Committee Report.¹ In Section III.(b) of the present Report, Table LXVIII, gives comparative results for nitrogen by two methods in a series of thirteen alloy steels, which show, in nine cases, average vacuum fusion figures slightly lower than the chemical results. Whilst it must be pointed out that the margin of difference between the two methods is no greater than the variations in nitrogen content reported by different co-operators using chemical methods only, the Sub-Committee nevertheless realise the possibility of slightly lower vacuum fusion results with certain alloy steels.

In explanation of these facts, it would appear that, whilst the nitrogen compounds in steel are decomposed by good vacuum fusion

¹ Third Report of the Oxygen Sub-Committee, *loc. cit.*, p. 309 P.

technique, involving high vacuum, the nitrogen is evolved from certain steels only with difficulty. Prolonged evacuation at low pressure, after removal of oxygen-bearing gases, is required to ensure complete separation. Reference to results by the fractional method shows that, with almost all steels, the bulk of the nitrogen is invariably found in the final (alumina) fraction, thus indicating the stability of certain nitrogen compounds. It is believed that the lowest pressure attained by a particular apparatus affects the facility with which nitrogen is evolved, so that certain apparatus, depending on the pumping equipment employed, are affected to a greater degree. In corroboration of these observations, the results given in Table XXII. are reported.

TABLE XXII.—*Comparison of Nitrogen Values found by Vacuum Fusion and Chemical Methods.*

Acid Open-Hearth Steel: 3.0% nickel, 0.8% chromium, 0.6% molybdenum.

Sample No.	Nitrogen. %.			
	Vacuum Fusion Method.	Chemical Method.	Difference.	Mean Difference.
1	0.004	0.006	0.002	} 0.001 ₅
2	0.004 ₅	0.006 ₅	0.002	
3	0.005	0.006	0.001	
4	0.003 ₅	0.005	0.001 ₅	
5	0.003 ₅	0.005	0.001 ₅	
6	0.004	0.004 ₅	0.000 ₅	

Following a vacuum fusion melt comprising six samples, all of 3% nickel-chromium-molybdenum steel, "chemical" nitrogen was determined on millings taken from the cooled melt, which analysed 0.001₅% of nitrogen. This value approximated very closely to the difference between the chemical and vacuum fusion results shown in Table XXII.

In respect to nitrogen determination, the position of the vacuum fusion method may be summarised in the statement that it represents a satisfactory method of determination. The results obtained compare favourably with those obtained by the chemical method when the latter is operated under the best conditions. In fact, results obtained for nitrogen by vacuum fusion have indicated possible errors in commonly accepted chemical methods of determination.

(c) *THE CHEMICAL DISTILLATION METHOD.*¹

BY T. SWINDEN, D.MET. (CHAIRMAN OF THE SUB-COMMITTEE).

SYNOPSIS.

A brief outline of the development and modifications in procedure recommended for the chemical determination of nitrogen in iron and steel is given and comparison made of the results obtained by co-operators using different procedures on typical alloy steels. The influence of composition, *i.e.*, presence of certain alloying elements, and of the physical condition of the sample on the simpler solution method is demonstrated and discussed. A tentative standard method is very fully described together with notes and recommendations, illustrated in many cases by practical experience. The future development of chemical methods is discussed.

Nitrogen in iron and steel is most commonly determined by a chemical method in which the sample is decomposed by an acid solution, the nitrogen being converted to ammonia, which is retained in the iron solution as an ammonium salt. By adding the acid solution containing the ammonium salt to an alkali and distilling, the ammonia is collected in the distillate and measured by one of two procedures, either (a) colorimetrically or (b) by an acid titration. Although the method appears to be quite straightforward, requiring little special apparatus and being easily adapted to routine needs, it has been the subject of a voluminous literature since its inception over seventy years ago. The main point, concerning which differences of opinion have been expressed, is in the acid and conditions employed for the decomposition of the sample and its nitrogen-bearing constituents. It will be recalled that, in the previous sub-section dealing with the determination of nitrogen by the vacuum fusion method, attention was directed to certain cases where the latter method gave higher nitrogen figures than the conventional chemical method. The apparent failure of the chemical method is due, undoubtedly, to incomplete decomposition of the nitrogen constituents by the initial acid attack, and a brief account of some of the solvents or methods which have, from time to time, been recommended for this purpose might usefully be given here.

Determinations of the nitrogen content of organic substances have been carried out by many chemists, including Davy, Berzelius, Gay-Lussac, Dumas, Liebig and others, using a variety of methods; among the earliest workers to apply the chemical method outlined in the previous paragraph to iron and steel was Boussingault,² who, determining the ammonia in the distillate by titration, obtained results on pig iron and steel of the order of 0.0045–0.0086% of

¹ Received January, 22, 1943.² Boussingault, *Comptes Rendus*, 1861, vol. 53, p. 77; *Zeitschrift für analytische Chemie*, 1862, vol. 1, p. 112.

nitrogen. This investigator noticed in his tests an acid-insoluble residue, which he separated and analysed for its nitrogen content by a soda-lime fusion method used extensively in organic analysis. Allen¹ applied to the distillation method the colorimetric finish *via* Nessler's reagent. Much of this early work of Boussingault and others was vitiated by excessive "blank" troubles. Later investigators have also remarked on the insoluble residue and have stressed the need for its complete decomposition for a full account of the nitrogen content. Among those acid-insoluble nitrogen constituents of steel believed by these workers to interfere with the acid solution method were the nitrides of silicon, aluminium, vanadium and titanium; in practically all cases in this early work, the insoluble residue was separated and treated by a fusion.

With the object of minimising the occurrence of the insoluble residue, different acid solvents have been recommended. Kjeldahl's method,² published in 1883, for the determination of nitrogen in organic matter consists in decomposing the sample by concentrated fuming sulphuric acid, to form ammonium sulphate. Later workers, on finding that certain organic substances were not completely decomposed by boiling sulphuric acid, increased its boiling point and the temperature of the reaction by an addition of potassium sulphate, and also described the need for a metallic catalyst to assist the oxidation of carbonaceous matter. These solvents have also been applied to the decomposition of steel with varied success. Decomposition with sulphuric acid and potassium bisulphate is said to give good results, but a usual practice has been that of dissolving the sample initially with dilute mineral acid, filtering the residue on asbestos and treating this residue with a fuming sulphuric acid/potassium-bisulphate mixture, although Johnson³ recommended a mixture of sulphuric and perchloric acids for this purpose. Mixtures of sulphuric and perchloric acids have also been recommended for the initial dissolution of the sample to avoid the necessity for a separate treatment of an insoluble residue. The use of sulphuric acid and phosphoric acid in the presence of selenium to obtain complete decomposition has been described by Brown,⁴ and Cunningham⁵ has suggested the use of hydrochloric acid followed by a little hydrofluoric acid.

It can thus be seen that choice of procedure for the decomposition of steel samples is very varied, and for this reason the Subcommittee felt that, in view of their interest and experience in the content of gases in metals, some guidance on recommended chemical procedure for nitrogen determination should be given.

¹ Allen, *Journal of The Iron and Steel Institute*, 1879, No. II., p. 480.

² Kjeldahl, *Zeitschrift für analytische Chemie*, 1883, vol. 22, p. 366.

³ Johnson, *Iron Age*, 1934, vol. 134, July 26, p. 10.

⁴ Brown, "Sampling and Analysis of Carbon and Alloy Steels," p. 292. New York, 1938: Reinold Publishing Co.

⁵ Cunningham, *Industrial and Engineering Chemistry, Analytical Edition*, 1939, vol. 11, p. 303.

TABLE XXIII.—*Summary of Nitrogen Results in the Alloy-Steel Series by Vacuum Fusion and Chemical Methods.*

No.	Type of Steel.	Co-operating Laboratory. ¹	Nitrogen. %.	
			Vacuum Fusion Method.	Chemical Method.
1	0.15% Aluminium.	B.F.R.L.	0.006	0.005 ₅
		C.R.D.	0.004 ₅	0.006 ₅
		I.C.I.	...	0.007
		N.P.L.	0.005 ₅	0.007
		Mean value	0.005 ₅	0.006 ₅
2	0.5% Aluminium.	B.F.R.L.	0.004 ₅	0.004 ₅
		C.R.D.	0.004	0.005
		I.C.I.	...	0.005
		N.P.L.	0.004	0.004
		Mean value	0.004	0.004 ₅
3	0.15% Aluminium, 0.01% nitrogen.	B.F.R.L.	0.012	0.013 ₅
		C.R.D.	0.009 ₅	0.012 ₅
		I.C.I.	...	0.013
		N.P.L.	0.010	0.010
		Mean value	0.010 ₅	0.012
4	3% Chromium, 0.6% molybdenum.	B.F.R.L.	0.010	0.009 ₅
		C.R.D.	0.010 ₅	0.011 ₅
		I.C.I.	...	0.010 ₅
		N.P.L.	0.010 ₅	0.012
		Mean value	0.010 ₅	0.011
5	6% Chromium, 0.6% molybdenum.	B.F.R.L.	0.018 ₅	0.018
		C.R.D.	0.019	0.019
		I.C.I.	...	0.020
		N.P.L.	0.015 ₅	0.023
		Mean value	0.017 ₅	0.020
6	13% Chromium.	B.F.R.L.	0.019	0.019
		C.R.D.	0.017	0.020
		I.C.I.	...	0.020
		N.P.L.	0.020	0.020
		Mean value	0.018 ₅	0.012
7	3.5% Nickel, 0.7% chromium.	B.F.R.L.	0.010	0.010
		C.R.D.	0.011	0.010 ₅
		I.C.I.	...	0.010
		N.P.L.	0.010	0.012
		Mean value	0.010 ₅	0.010 ₅
8	4.5% Nickel, 1.25% chromium.	B.F.R.L.	0.010	0.008
		C.R.D.	0.008 ₅	0.012 ₅
		I.C.I.	...	0.007
		N.P.L.	0.010	0.010
		Mean value	0.009 ₅	0.009 ₅

TABLE XXIII. (*continued*).

No.	Type of Steel.	Co-operating Laboratory. ¹	Nitrogen. %.	
			Vacuum Fusion Method.	Chemical Method.
9	2.5% Nickel, 0.75% chromium, 0.50% molybdenum.	B.F.R.L.	0.004	0.003 ₅
		C.R.D.	0.005 ₅	0.005
		I.C.I.	...	0.004 ₅
		N.P.L.	0.003	0.003
		Mean value	0.004	0.004
10	6% Tungsten, 0.6% carbon.	B.F.R.L.	0.007	0.007 ₅
		C.R.D.	0.007	0.006 ₅
		I.C.I.	...	0.006 ₅
		N.P.L.	0.006 ₅	0.007
		Mean value	0.007	0.007
11	1.2% Manganese, 0.25% molybdenum.	B.F.R.L.	0.002 ₅	0.004
		C.R.D.	0.005 ₅	0.007
		I.C.I.	...	0.006 ₅
		N.P.L.	0.004	0.007
		Mean value	0.004	0.006
12	18% Chromium, 8% nickel.	B.F.R.L.	0.012	0.012
		C.R.D.	0.010 ₅	0.014 ₅
		I.C.I.	...	0.015
		N.P.L.	0.011 ₅	0.014
		Mean value	0.011 ₅	0.014
13	13% Manganese, 1% carbon.	B.F.R.L.	0.005 ₅	0.010
		C.R.D.	0.011	0.014 ₅
		I.C.I.	...	0.014 ₅
		N.P.L.	0.008	0.011
		Mean value	0.008	0.012 ₅

¹ B.F.R.L. = Brown-Firth Research Laboratories.

C.R.D. = Central Research Department, The United Steel Companies, Ltd.

I.C.I. = I.C.I. (Alkali), Ltd.

N.P.L. = National Physical Laboratory.

Comparison of Nitrogen Results on Typical Alloy Steels.

Table XXIII. (which is a reproduction of Table LXVIII. of Section III.(h)) gives the nitrogen contents, as obtained by the vacuum fusion and chemical methods, of a series of thirteen steels, including a selection of typical present-day alloy steels. These steels contain aluminium, manganese, nickel, chromium, tungsten and molybdenum and have been made by commercial methods, *i.e.*, open-hearth, high-frequency or electric-arc processes.

Whilst it is not suggested that this series of alloy steels is entirely comprehensive, it is representative of many types of carbon and alloy steels in general use to-day. Examination of the results shows that,

TABLE XXIV.—Comparison of Methods used for Chemical Determinations of Nitrogen on the Thirteen Alloy Steels.

Co-operating Laboratory :	Brown-Firth Research Laboratories.	Central Research Department, The United Steel Companies, Ltd.	I.C.I. (Alkali), Ltd. (Northwich).	National Physical Laboratory.
Weight of sample.	1.0 g.	1.0 g.	2.0 g.	5.0 g.
Solvent method.	5 ml. sulphuric acid (sp. gr. 1.84), 5 ml. water, followed by fuming for 20 min.	5 ml. sulphuric acid (sp. gr. 1.84), 25 ml. water, followed by fuming for 10 min.	30 ml. hydrochloric acid (1:1). Heat gently on water-bath until volume reduced to 20 ml.	25 ml. hydrochloric acid (sp. gr. 1.16).
Dilution prior to addition to alkali.	25 ml. water.	40 ml. water.	30 ml. water.	25 ml. water.
Alkali used.	300 ml. 5% caustic soda.	300–350 ml. 5% caustic soda.	300–350 ml. 3% caustic soda.	Lime emulsion; 25 g. in 500 ml. water.
Amount of water distilled during test.	100 ml.	150–200 ml.	200 ml.	250 ml.
Time of distillation.	30 min.	45 min.	35 min.	45 min.
Absorbent.	Water.	Water.	10 ml. N/100 hydrochloric acid.	Measured excess N/20 sulphuric acid.
Measurement of ammonia.	Colorimetric, using Nessler reagent.	(a) Volumetric, using N/200 acid and mixed indicator of methylene blue and methyl red. (b) Colorimetric, using Nessler reagent.	Volumetric, using N/100 caustic soda and mixed indicator as at C.R.D.	Volumetric, using N/20 caustic soda and methyl red as indicator.

with the exception of one or two steels, notably Nos. 8, 11 and 13, agreement in the chemical determinations carried out by the different laboratories is satisfactory. This conclusion is gratifying in view of the different techniques employed, a detailed summary of which is given in Table XXIV.

The four methods outlined in Table XXIV. differ in several essential details :

- (1) Decomposition of sample.
- (2) Type of alkali used in the distillation.
- (3) Measurement of the ammonia in the distillate.

It will be noticed also that in none of these methods was resort made to filtration and subsequent treatment of any insoluble residue, and the good agreement obtained must be ascribed to either of two explanations :

(a) That, although these steels are representative of a number of present-day alloy steels (with a notable exception—titanium steels), all the nitrogen-bearing compounds are soluble in either hydrochloric or sulphuric acids.

(b) That, if these steels contain acid-insoluble nitrogen-bearing constituents, they are decomposed by the subsequent digestion in the alkali solution.

The second explanation accords with the view of Jordan and Swindells,¹ who stated that part, at least, of the nitrides in the undissolved residue is decomposed by boiling soda solution to form ammonia.

Further Comparative Nitrogen Determinations on Alloy Steels.

In spite of the closeness of the agreement in the examination of the thirteen alloy steels, it was felt by certain Members of the Sub-Committee that, in respect of the four procedures outlined in Table XXIV. and particularly the two using hydrochloric acid as solvent, the choice of steels had been fortuitous and such universal applicability did not hold for all alloy steels. In particular, one notable omission from this series of alloy steels is the well-known austenitic chromium-nickel steel containing titanium, which gives rise to a stable nitrogen compound. The occurrence and the effect of this stable titanium-nitrogen compound on the chemical method for the determination of nitrogen had been observed several years ago by many investigators, notably Johnson and Cunningham, and, moreover, in 1934–35 this effect was encountered in The United Steel Companies, Ltd., Central Research Department during a study of the modes of occurrence of titanium in austenitic steels. This work had shown quite clearly that treatment of the sample with dilute hydrochloric

¹ Jordan and Swindells, *Journal of the U.S. Bureau of Standards*, 1922, vol. 18, p. 18.

acid resulted in incomplete decomposition of the titanium-nitrogen-bearing compounds and consequently low values for the nitrogen content. At that time a method had been evolved for such steels, depending on decomposition with mixed sulphuric and perchloric acids, followed by fuming under an air condenser. However, even with this decomposition, full recovery was obtained only after reduction of the steel solution with metallic zinc prior to the distillation over alkali. The necessity for this treatment would infer that the drastic conditions of the decomposition lead to the formation of certain oxidised nitrogen compounds which require reduction with nascent hydrogen for complete conversion to ammonium salt. Later work with the method offers some confirmation of this conclusion, in that the degree and period of fuming appear to influence the results,

TABLE XXV.—*Analyses of Samples Examined for Nitrogen Content.*

Element.	Sample A.	Sample B.	Sample C.
Carbon. %	0.145	0.35	0.10
Manganese. %	0.34	0.49	0.78
Silicon. %	0.63	0.23	1.07
Nickel. %	8.02	4.42	8.00
Chromium. %	18.44	1.38	18.28
Tungsten. %	0.33
Titanium. %	0.59	...	0.61
Molybdenum. %	0.39	...

which are higher with a more gentle, shorter fuming period than with a prolonged, vigorous fuming, and it is suggested that these conditions lead to greater formation of these oxidised and volatile nitrogen compounds. However, this method has been used for a number of years, but it is subject to a comparatively high "blank" and work has been directed recently to a simpler technique which should ultimately prove satisfactory for such steels.

Since, in the Sub-Committee's opinion, it is very desirable that the proposed standard method for the nitrogen content of steel should be equally applicable to as many types of steel as possible, the interference of titanium on the chemical determination, using hydrochloric acid for the initial decomposition, had to be established beyond doubt. Accordingly, nitrogen determinations on two common types of titanium-bearing steels have been carried out by a small panel of the Sub-Committee. In addition, a nickel-chromium-molybdenum steel was included in these experiments, since one Member of the Sub-Committee had noticed from time to time difficulties with such steels. The analyses of these steels and the results of the nitrogen-determination experiments are given in Tables XXV. and XXVI., respectively.

Viewing the results in Table XXVI. collectively, the following comments are made :

(a) The presence of titanium in steel modifies the form of occurrence of the nitrogen compounds, so that incomplete decomposition results by the normal hydrochloric acid treatment of the sample, and no variation of this treatment leads to better decomposition and recovery of the nitrogen content. The use of sulphuric acid followed by subsequent fuming for a period of about 15 min. gives more satisfactory decomposition of the nitrogen-bearing compounds and consequently leads to higher nitrogen values on distillation.

TABLE XXVI.—*Results of Nitrogen Determinations on the Three Steels in Table XXV.*

Laboratory.	Procedure.	Nitrogen. %.		
		Sample A.	Sample B.	Sample C.
N.P.L.	Procedure as outlined in Table XXIV. 5-g. sample dissolved in hydrochloric acid. Distilled over lime. Titration with <i>N</i> /20 acid solution.	{ 0.003 0.004 }	0.008	0.004
B.F.R.L.	1-g. sample. Distilled over caustic soda. Colorimetric measurement. Decomposition of sample as below :			
	(a) 20 ml. hydrochloric acid (1 : 1) heated on water-bath.	0.002 _s	0.006 _s	0.006 _s
	(b) 30 ml. hydrochloric acid (1 : 4) heated to low bulk on hot-plate.	0.002 _s	0.008 _s	0.006 _s
	(c) 20 ml. hydrochloric acid (1 : 1) + 0.5 ml. hydrofluoric acid heated on water-bath.	0.006
	(d) 5 ml. sulphuric acid fumed for 5 min.	0.004 _s	0.008 _s	0.011 _s
	(e) 5 ml. sulphuric acid + 3 g. potassium bisulphate fumed for 5-10 min.	0.002 _s	0.007	0.012 _s
C.R.D.	(f) 5 ml. sulphuric acid + 3 g. potassium bisulphate fumed under air condenser for 30 min.	0.007 _s 0.007	0.008	0.011 _s
	1-g. sample. Distilled over caustic soda. Volumetric determination using <i>N</i> /200 hydrochloric acid. Decomposition as below :			
	(a) 20 ml. hydrochloric acid (1 : 1) digested on hot-plate.	0.002 _s	0.009 _s	0.003
	(b) 6 ml. sulphuric acid fumed under condenser for 5-10 min.	0.007	0.010 _s	{ 0.009 _s 0.009 0.012 0.010 }
	(c) 6 ml. sulphuric acid + 3 g. potassium bisulphate fumed under condenser for 5-10 min	

(b) The results obtained with sample *B* show that the deleterious effect of molybdenum, noticed with certain samples at various times, was not evident with this particular sample, since equally good results were obtained with both hydrochloric- and sulphuric-acid methods of decomposition. The results on the thirteen alloy steels by the four co-operators (*see* Table XXIII.) confirm this conclusion, and it is probable that the variability of response of certain molybdenum steels to the hydrochloric-acid solution method may be connected with the physical condition of the sample. This conclusion is borne out

by the following investigation into the cause of the rather wider variation of results on the alloy steel No. 8.

The chemical nitrogen results on alloy steel No. 8, which is a 4½% nickel-chromium steel of the air-hardening type, show the greatest deviation in the entire series, and it was felt that this difference had a definite significance, since both the highest result, 0.0125% by C.R.D., and the lowest, 0.007% by I.C.I., had been amply confirmed in the two individual laboratories. One difference in the two procedures lay in the solvent selected for the initial solution (*see* Table XXIV.), but this was not considered vital in view of the good agreement with the other low-alloy steels. Consideration of all the factors revealed a further difference, in that the I.C.I. results had been obtained on millings taken from a softened piece of bar, whereas C.R.D. had milled the bar as received, *i.e.*, in the air-hardened condition. Consequently the following experiments were carried out to investigate the effect of this difference.

A short length of bar No. 8 was annealed at 650° C. for 2 hr. and cooled slowly, and determinations were made on millings from this and from the hardened bar. The results were very revealing, a *high result of the order of 0.012–0.013% of nitrogen being obtained on the hard bar using both hydrochloric and sulphuric acids as solvent*, whilst both procedures yielded low results of the order of 0.004–0.006₅% of nitrogen on the annealed bar. Two possible explanations of this fact were suggested :

(a) Owing to the extremely hard nature of the as-received bar, the milling process was accompanied by an adsorption of atmospheric nitrogen on the surface of the millings, giving a high result.

(b) As a result of the annealing process, the nitride, which was either in solution or in a finely divided state in the hardened bar, was thrown out of solution and coalesced with the carbide, so that, after solution in acid, an insoluble residue of carbide and nitrogen compounds was obtained. On this hypothesis the lower result would be erroneous.

These theories were investigated in subsequent tests. Similar determinations on single solid pieces of bar weighing 2 g. confirmed the differences between the two bars, thereby supporting the second suggestion. Vacuum fusion determinations gave equal results for both bars, again supporting the second view. The insoluble residues resulting from further determinations with hydrochloric acid as solvent were separated and analysed for nitrogen. The annealed bar gave the greater residue, having a nitrogen content of 0.012%; the residue of the hard bar was slight and showed only a trace of nitrogen. Finally, similar high results on both bars were obtained by the proposed standard method (*see later*). The full results are included in Table XXVII.

The results in Table XXVII. clearly indicate that annealing of this sample induces a change in the mode of occurrence of the nitrogen, whereby an acid-insoluble compound is formed and low results follow by the usual hydrochloric-acid solution method. Full recovery of the nitrogen content is, however, obtained by the proposed standard procedure. This conclusion is of extreme importance, since it seriously limits the applicability of the hydrochloric acid method, particularly to the analysis of steels of unknown origin and condition.

TABLE XXVII.—*Nitrogen Results on Alloy Steel No. 8.*

(Determinations at Central Research Department, The United Steel Companies, Ltd.)

Procedure.	Nitrogen. %.			
	Hardened Bar. V.P.N. 527.		Annealed Bar. V.P.N. 285.	
(a) Millings.				
(1) Hydrochloric acid.	0.013 ₅	0.013	0.004	0.003 ₅
	0.012 ₅	0.012		0.004 ₅
(2) Sulphuric acid.	0.013 ₅	0.012 ₅	0.006 ₅	0.006 ₅
	0.013	0.013 ₅		0.006
(b) Solid piece.				
Sulphuric acid.		0.013		0.007
(c) Millings.				
Solution in hydrochloric acid.	Filtrate	0.012 ₅	Filtrate	0.002 ₅
Residue collected, fumed	Residue	Nil	Residue	0.012
with sulphuric acid and	Total	0.012 ₅	Total	0.014 ₅
potassium bisulphate.				
(d) Millings.				
Proposed standard method.		0.013 ₅		0.012
Fumed strongly with sulphuric		0.013		0.011 ₅
acid and potassium bisul-				
phate.				
(e) Vacuum fusion.		0.009 ₅		0.009

Proposed Tentative Method for the Determination of Nitrogen in Iron and Steel.

In view of the foregoing conclusions with respect to the physical condition of the sample, together with the interference of titanium (and possibly other elements such as zirconium and vanadium) in the simple chemical method, a standard procedure applicable to all possible cases is formulated below.

Since the sulphuric acid method of decomposition affords the wider applicability, this method is suggested as the basis of the proposed standard procedure. At the same time, it must be

conceded that, with the vast majority of present-day commercial steels, the usual hydrochloric-acid solution method will, in many cases, yield results of a comparable order, if due regard is paid to the physical condition of the sample.

(a) *Apparatus Required.*

No special apparatus is required other than the normal laboratory ware. The apparatus, described by Jones and Morgan¹ and illustrated by the author,² forms a convenient arrangement, and has been used consistently with little modification over a long period. The distillation flask has a capacity of 750 ml. and the adaptor leading to the receiver has been modified by the insertion of a safety bulb of about 100 ml. capacity. The side arm of the distillation flask is passed through a cork into the cooling part of the water-condenser, so avoiding condensation around the cork connection between the side arm and condenser. A battery of six such apparatus has been set up on one common heating tray and determinations are carried out in batches. Other co-operators use distillation assemblies of interchangeable glass-joint units, with excellent results. As mentioned earlier, normal laboratory apparatus can be used, but a ground joint between the distillation flask and the tap-funnel delivery tube is definitely advisable, whilst the all-glass-joints assembly probably gives the maximum safety from external contamination. No grease need be used with these ground-glass-joint assemblies, as water forms an adequate seal, and the apparatus may be finally cleaned after fitting up by allowing uncondensed steam to pass for a few minutes before connecting the condenser to the cooling-water supply.

The decomposition of the sample is conveniently carried out in a small 250-ml. round-bottom flask fitted by a ground joint to an air-condenser about 18 in. in length.

(b) *Procedure.*

Dissolve 1 g. (or 2 g.) of sample in 25 ml. of dilute sulphuric acid (1 : 4) in the small flask mentioned above. Add 2 g. of potassium bisulphate, A.R., close the flask with a cover and heat over a small flame or electric hot-plate until the solution is almost fuming (see note d(3) below). Attach the air-condenser and fume for at least 15 min. Cool and dilute with 30 ml. of water.

While solution of the sample is taking place, add to the distillation flask 75 ml. of 20% caustic soda solution and 400 ml. of water, together with a few pieces of silica brick or glass tube (to prevent

¹ Jones and Morgan, *The Iron and Steel Institute, Carnegie Scholarship Memoirs*, 1932, vol. 21, p. 39.

² Swinden and Stevenson, Sixth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1935, *Special Report No. 9*, Section VI., p. 111.

bumping), and boil the solution over a small flame or electric heater (see note *d*(4)). Collect the distillate and test successive 40-ml. portions for the presence of ammonia by Nessler reagent. Continue the distillation until no trace of ammonia is detected in the condensate; at this stage, the volume remaining in the distillation flask will be approximately 300–350 ml. Insert the adaptor into a clean receiving flask containing a very small quantity of water so that the outlet just dips below the liquid surface.

Transfer the acid solution to the tap-funnel and slowly run it into the boiling soda solution at a rate which maintains the boiling of the soda solution, rinsing the funnel with small additions of water. Continue the distillation for about 45 min. (see note *d*(5)), (with high nitrogen contents of the order of 0.3%, &c., a longer boiling period may be required), during which time about 150–200 ml. of water are collected. Determine the ammonia content by one of the alternative procedures given below.

(1) *Colorimetric Determination*.—To the distillate and to an equal volume of ammonia-free water containing a measured quantity of standard ammonium chloride solution approximating to the ammonia content of the distillate, add 2 ml. of Nessler reagent. Allow both solutions to stand for 15 min. in order to develop fully the colour and compare the intensities of the two coloured solutions by dilution of the more intense solution (see note *d*(6)).

(2) *Volumetric Determination*.—To the distillate add four drops of mixed indicator and titrate the solution with *N*/200 hydrochloric acid.

1 ml. of *N*/200 hydrochloric acid = 0.00007 g. of nitrogen.

(c) Solutions Required.

(1) *Dilute Sulphuric Acid* (1 : 4).—To 750 ml. of ammonia-free water add 250 ml. of sulphuric acid (sp. gr. 1.84). Different consignments of sulphuric acid vary considerably in respect to contamination by nitrogen compounds, particularly nitric acid, hence close inspection of each separate "winchester" quart bottle is advisable. A delicate test for nitrates is afforded by brucine, which when dissolved in concentrated sulphuric acid, gives an orange-to-pink colour in the presence of nitrates. It is advisable, therefore, to apply this test to a number of sulphuric acid winchesters, reserving solely for use with the nitrogen method that winchester showing the lowest nitrate content with the brucine reagent. One Member of the Sub-Committee prefers to redistill the concentrated sulphuric acid for the nitrogen method, and this precaution is recommended in order to minimise "blank" troubles still further.

(2) *Ammonia-Free Water*.—All water used in this method must be ammonia-free water collected by redistillation over caustic soda containing an oxidant. In many cases thoroughly boiled distilled water, which can often be prepared free from ammonia, serves the

purpose effectively. However, this practice is often dangerous, leading to excessive " blank " troubles.

One Member of the Sub-Committee has in constant operation a stainless-steel boiler of about 10 litres capacity connected to a condenser. Ordinary distilled water is redistilled over 20 g. of caustic soda and 1 g. of potassium permanganate until successive runnings are ammonia-free, the remaining distillate being then collected.

(3) *20% Caustic Soda*.—Dissolve 200 g. of stick caustic soda in hot water and dilute to 1000 ml. with ammonia-free water. Earlier investigators have stipulated that the hydroxide must be prepared from metallic sodium, but the stick qualities, both A.R. and ordinary, will be found quite suitable. Lower and possibly cheaper qualities of caustic soda should *not* be used. These grades of caustic soda contain nitrites and nitrates, which are reducible to ammonia by the addition of the dissolved iron solution prior to distillation. Thus, as with water, it is possible, and indeed it has occurred in the author's experience, for caustic soda from which no ammonia can be distilled to yield abnormal results on the addition of a steel sample.

(4) *Nessler Reagent*.—Dissolve 35 g. of potassium iodide and 12.5 g. of mercuric chloride in 200 ml. of ammonia-free water. To this solution add, with constant stirring, a cold saturated solution of mercuric chloride until a slight red precipitate remains, followed by an addition of 120 g. of caustic soda dissolved in 120 ml. of water. Finally add a little saturated mercuric chloride solution and dilute the volume to 1000 ml. with ammonia-free water. Allow the solution to stand for several hours and filter before use.

(5) *Standard Ammonium Chloride Solution*.—Dissolve 0.0382 g. of ammonium chloride, A.R., in ammonia-free water and dilute to 1000 ml.

1 ml. of this solution = 0.00001 g. of nitrogen.

(6) *Hydrochloric acid, N/200*.—Dilute 50 ml. of N/10 hydrochloric acid to 1000 ml. with ammonia-free water.

1 ml. of N/200 hydrochloric acid = 0.00007 g. of nitrogen.

(7) *Indicator Solution*.—Dissolve 0.125 g. of methyl red and 0.083 g. of methylene blue in 100 ml. of a mixture of spirits of wine and absolute alcohol (1 : 1) by digesting at 70° C. for 2 days.

(d) *Notes on the Procedure.*

(1) Every precaution against accidental contamination with extraneous ammonia must be taken. Among the points to watch in addition to those outlined under the heading of " Solutions Required " are :

(a) The determinations should be carried out in an atmosphere free from ammonia, this condition usually being fulfilled

by the use of a small laboratory removed from the main laboratory or stock rooms.

(b) All solutions, reagents and apparatus used should be stored in the room used for the determinations. Solutions are best kept in bottles with fume caps.

(c) Laboratory overalls frequently absorb ammonia fumes if worn for any length of time in the main laboratory, resulting in accidental contamination. Specially clean overalls should therefore be worn by operators.

(d) All apparatus should be thoroughly cleaned and rinsed with ammonia-free water. Grease contamination should be avoided.

(e) The actual sample must be thoroughly washed with water and organic solvents to remove possible ammonia and grease films.

(2) Frequent "blank" determinations are necessary. These are best done by concurrent determinations on a standard steel and by distillations of a measured volume of ammonium chloride in the presence of the ferrous hydroxide remaining from a previous determination. One Member of the Sub-Committee, carrying out determinations in batches of six, conducts a standard steel determination with each series.

(3) The fuming of the sulphuric acid solution is conveniently carried out either by heating over a short, widely spread flame of the mushroom type, so that the flame does not impinge on the flask, or on an electric hot-plate.

(4) Bumping of the distilling solution can be minimised by the usual method of a small addition of silica brick, but this occurrence is connected more with the type of heating employed. A mushroom type of burner with a short, widely spread flame about 1 in. below the flask reduces bumping very effectively, and, moreover, it has been noticed that the distillation flasks, which frequently failed due to pin-hole attack when the normal type of burner was used, last for a much longer period with the mushroom type of flame. An electric heater arranged to heat the flask largely by radiation serves the same purpose.

(5) Under conditions of steady boiling in a 750-ml. distillation flask, the whole of the ammonia from normal steels is expelled in 30 min.; hence a standard time of 40–45 min. should be employed.

(6) The full colour intensity of the Nesslerised ammonia solution is developed only after about 15 min., and, moreover, varying tints are often obtained on distillates from different classes of steel, the variation being connected in some way with the carbon content. Again, variation in tint is often produced by the addition of ammonium chloride to a solution already containing Nessler reagent. Hence, comparison is best made by adjusting the standard so that the standard and the test have almost identical ammonia contents

before addition of the Nessler reagent, the final comparison being made by dilution of the more coloured solution. The comparison may be made by direct visual observation, by any of the well-known colorimeters, or by one of the more recent types of photometer. Using the photometer, it is necessary only to determine the light absorption of the distillate in a particular wave-band and by reference to a previously determined calibration chart of light absorption against ammonia concentration, to obtain the nitrogen content of the distillate.

Future Development of Chemical Methods.

The chemical method can be subdivided into two main operations :

- (a) The decomposition of the sample.
- (b) The collection and measurement of the ammonia.

The bulk of previous work has been directed towards obtaining more complete decomposition of the sample, and in the Sub-Committee's experience many of the more involved procedures, such as initial solution in dilute acid followed by filtration through asbestos and digestion of the residue in mixtures of high-boiling-point acids, are unnecessary. For most steels the same object can be achieved by digestion of the original sample in sulphuric acid. It must, however, be pointed out that with highly complex alloys separate treatment of an acid-insoluble residue may be necessary and is in fact desirable.

The method of collection and measurement of the ammonia is likely to afford scope for improvement. Whilst the principle of normal distillation over caustic soda has been the standard practice for many years, recent investigators¹ have proposed a steam distillation which considerably reduces the time required for the complete removal of the ammonia. Whilst this will effect some saving of time, it is perhaps not of such importance where batch determinations are conducted, since the decreased time of distillation would limit considerably the number of apparatus which could be operated by one chemist and the net improvement would be very small. This method does, however, affect the weight of sample taken, thereby improving the accuracy of the nitrogen determination, in so far as bumping troubles due to increased weight are minimised. It is perhaps on these lines that future development will take place.

Finally, one must not overlook the possibility of the development of a technique whereby the distillation can be entirely omitted, using, for example, a colorimetric principle applicable to nitrogen in the presence of iron and the usual steel elements.

¹ Kempf and Alresch, *Archiv für das Eisenhüttenwesen*, 1939-40, vol. 13, p. 419.

Section III.—Examination of Materials.

(a) *THE PRODUCTION OF OXYGEN-FREE IRON BAR.
N.P.L. IRON, MARK 2.*¹By H. A. SLOMAN, M.A., AND A. J. COOK (THE NATIONAL PHYSICAL
LABORATORY, TEDDINGTON).

(Under the direction of C. Sykes, D.Sc., F.R.S.)

(Figs. 7 to 10 = Plate XVIII.)

SYNOPSIS.

This paper describes the experimental technique developed at the National Physical Laboratory for the production of low oxygen content iron bar, classified as N.P.L. Iron, Mark 2. The starting material was high-quality electrolytic sheet, and a detailed account is given of the operations necessary to obtain an economic maximum of $\frac{1}{2}$ -in. dia. bar from hydrogen-treated furnace-cooled ingots. The requisite hot-working and cold-rolling of this metal were not without difficulties, which have been successfully overcome. Routine checking at different stages of the process has been accomplished by X-ray examination together with vacuum fusion and chemical analyses.

In order to investigate some important fundamental aspects of certain of the methods for the determination of oxygen in steel under examination by the Oxygen Sub-Committee, the need arose for a quantity of pure iron which should be substantially free from oxygen and preferably in the form of $\frac{1}{2}$ -in. dia. rolled bar. The National Physical Laboratory undertook to provide about 50 lb. of such material for the use of Members of the Sub-Committee.

Considerable experience had already been obtained in the Metallurgy Department, National Physical Laboratory, of the preparation of high-purity iron, first on a small scale² and later on a large laboratory scale,³ and the method of deoxidation by treatment with hydrogen in the molten state was well established. Not a great deal of work had, however, been carried out on the subsequent working of the metal into small-diameter bar. The method employed in the present case was based on this past experience, and the starting material—namely, electrolytic iron sheet—was the same, but since small amounts of impurities, other than oxygen, could be tolerated, it was possible to by-pass the rather lengthy process of conversion, first to ferrous chloride, then to iron oxide and sponge iron, which had been previously adopted for their removal.³ It was decided to designate the present iron as "N.P.L. Iron, Mark 2," in order to distinguish it from other oxygen-free iron prepared

¹ Received December 1, 1942.² Adcock and Bristow, *Proceedings of the Royal Society*, 1935, A., vol. 153, p. 172.³ Adcock, *Journal of the Society of Chemical Industry*, 1940, vol. 19, p. 28. 1943—ii

at the National Physical Laboratory and subjected to the intermediate process outlined above.

The electrolytic iron available was very consistent in composition, a typical analysis being given below :

Carbon	. 0.009%	Phosphorus	0.018%	Copper	. 0.011%
Silicon	. 0.0047%	Manganese	. 0.0003%	Magnesium	. 0.0024%
Sulphur	. 0.0008%	Nickel	. 0.0014%	Aluminium	. 0.001%

Melting Procedure.

All melting was carried out in a high-frequency induction furnace. First, the sheet was cut into strips and fed into an open porous magnesia crucible, producing a heavily oxidised ingot weighing about $3\frac{1}{2}$ lb. The objects of this preliminary melting were to obtain a solid ingot of the correct dimensions for the subsequent operations and also to produce an oxide slag into which some of the impurities would be fluxed and absorbed by the porous magnesia. The crucible, when cold, was easily broken away from the metal, which was then thoroughly cleaned by grinding all surfaces and examined for refractory inclusions. The heavily oxidised top layer was cropped if necessary and returned for remelting. The final deoxidising treatment consisted of melting two such ingots together in a sintered-alumina crucible (fired to about $1750^{\circ}\text{C}.$) and passing dry hydrogen over the liquid surface for some hours. Since no facilities were available for casting in a controlled hydrogen atmosphere, the metal was allowed to cool to room temperature in the crucible, giving an ingot about 2 in. in dia., 8 in. in length and weighing about 7 lb. In the absence of any control over the rate of cooling the shrinkage pipe in such an ingot may easily extend for 5 in. or 6 in. from the top, reducing the weight of solid metal suitable for subsequent working obtained from each treatment to about 2 lb. Such an output would be very uneconomical in time and material, and, accordingly, the scheme of controlled cooling, previously described,¹ was developed to a point which permitted an average of 6 lb. of solid metal to be obtained on each occasion.

Early experiments, besides showing the need for controlled cooling, indicated the importance of the cleaning of the surfaces of the ingots from the oxidising melt referred to above. It was found that when refractory inclusions were left, reaction occurred with the alumina crucible, the mixture of $\text{MgO-FeO-Al}_2\text{O}_3$ forming a non-reducible spinel which was retained as pockets in the surface, and occasionally in the interior, of the finished ingot. Such an erratic source of oxygen was obviously very undesirable. In the absence of these inclusions, the hydrogen-treated ingot showed no tendency to react with or adhere to the dense alumina crucible and presented a surface with a smooth bright finish.

The method adopted for the hydrogen treatment was modified

¹ Adcock, *loc. cit.*

in some respects from that previously described. After ensuring that the assembly was vacuum-tight, the metal was held at a temperature of 800–1000° C. for 1 hr. with a hydrogen stream, at a pressure of 15–20 cm. of mercury, passing through the furnace tube. The hydrogen was led directly to the surface of the metal by means of a narrow silica tube, which passed down the furnace tube to a hole centrally placed in the lid covering the crucible. The reaction products were swept away by excess hydrogen and extracted from the bottom of the furnace tube with a vacuum pump, protected by suitable drying agents. This preliminary treatment cleaned up the oxygen retained in the powdered refractory used to support and insulate the crucible as well as any remaining on the surface of the iron. The temperature was then raised to about 1600° C. and the metal held molten for 3–4 hr., the hydrogen stream impinging on the surface of the molten metal being maintained. It is probable that a shorter period of treatment would have sufficed, but this point was not thoroughly examined. At the end of this time the gas flow was reduced to approximately half in order to slow down the losses due to conduction, and the furnace tube was gradually lowered through the inductor coil until it was no longer possible, with maximum power, to maintain the top of the ingot molten. This normally occurred when about four-fifths of the ingot was below the bottom of the coil. The power was then cut off and the hydrogen flow maintained until the whole system was cold. Thus solidification was started at the bottom of the ingot while top feeding very largely eliminated the shrinkage cavity. As a result of experience a definite time schedule was evolved for the lowering operation and finally it became possible to produce ingots which gave about 6 lb. of solid metal free from cavities.

After removal from the crucible, each ingot was radiographed in two directions at right angles, in order to show the size and direction of the cavity, and was then cropped according to the evidence of the X-ray photograph. Figs. 7, 8 and 9 show three such photographs from different ingots. It should be noted that no cropping had been carried out when these photographs were taken. The first two are good, but in the third it will be seen that, while the amount of solid metal is similar to that in the ingot shown in Fig. 8, the form of the cavity is quite different. Experience proved that this type of cavity was produced when the metal which was feeding the pipe was not sufficiently hot, and, for reasons which will be discussed later, was to be avoided. Fig. 10 shows, for comparison, the shrinkage cavity in an ingot in which no control was exercised over the cooling; it will be seen from the position of the lower horizontal line that not more than a quarter of this ingot could be usefully employed.

From time to time chemical analyses were made on these ingots with particular reference to magnesium and aluminium to ensure that refractory materials had not been entrapped during the foregoing operations. A typical analysis is given below, which reveals

some improvement in certain of the impurities present in the original material :

Carbon	. 0.005%	Phosphorus	0.015%	Copper	. 0.0093%
Silicon	. 0.0018%	Manganese	Nil	Magnesium	. 0.0015%
Sulphur	. 0.001%	Nickel	. 0.0019%	Aluminium	. 0.0003%

Vacuum fusion determinations for oxygen were carried out on specimens machined from the cropped upper portion of each ingot. The results, which were consistently of the order 0.0002–0.0007% of oxygen, show that the hydrogen treatment employed produces iron substantially free from oxygen. (In Section III.(b) of this Report, evidence is given which suggests that this iron is in fact essentially free from internal oxygen and that the values found by vacuum fusion analysis represent oxygen on the surface of the analytical specimen.) The iron was also found to contain only a trace of nitrogen but an appreciable quantity of hydrogen. This latter was rapidly lost on standing or hot-working.

Specimens for microscopical examination were also taken but no oxide was ever visible, thus confirming earlier conclusions.¹ The remainder of each cropped portion was returned for remelting in hydrogen.

Forging and Rolling.

Owing to the method of cooling outlined above, the ingots were extremely coarse-grained and very brittle, being unable to withstand any form of cold-work. Hot-working was therefore essential, and the problem became one of developing a technique for the initial breaking-down of the large crystals which would not increase the oxygen content.

After many trials the following procedure was adopted : Each ingot was heated in air to 900–1000° C. in an induction furnace and quickly transferred to a power hammer, under which it was held with its long axis parallel with the anvil face. It was found impossible to forge in such a way as to maintain a circular section, as the metal always cracked. Accordingly, the section was "squared" by turning the ingot through a right angle between successive blows. Particularly in the early stages of reduction was it necessary to use the heaviest blow of which the hammer was capable, in order to avoid cracking. A useful criterion that the metal was withstanding the work was found in the appearance of the ends of the ingot, which, in successful operations, became more and more convex. Periodically, the ingot was reversed end-to-end, and it was arranged that these reversals should be sufficiently frequent to avoid the formation of a shoulder near the middle of the ingot. The metal was reheated when its temperature had fallen to about 700° C., care being taken not to prolong the working when the ingot had cooled

¹ Sloman, Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 311 p.

so as to "ring" under the hammer. The forging was continued down to about $1\frac{1}{8}$ in. square section, when the bar was shaped approximately round, finishing about 18–24 in. long and 1 in. in dia.

At this stage, the convex ends of each bar were cropped and oxygen determinations made on specimens machined from each end. Usually the results were identical with those obtained on specimens from the same ingot before forging, thus showing that hot-working does not increase the internal oxygen content. From time to time, however, it was noted that a specimen taken from that end of a bar which had been the top of the original ingot, *i.e.*, immediately below the shrinkage cavity, gave oxygen values far in excess of those normally obtained—for example, 0.02–0.03% instead of 0.0005%. When this type of trouble was encountered it was commonly found that consistently high oxygen values were obtained over a length of up to 6 in., beyond which the content would suddenly become normal and equal to that at the other end of the bar. Microscopical examination of cross-sections taken from these abnormal portions did not show any oxide particles, but revealed areas, usually near the centre of the section, where the grain boundaries showed an unresolvable thickening. This suggested that the trouble was due to minute fissures which had become oxidised but had welded sufficiently not to open into visible cracks. Since similar effects were never apparent at the other ends of the bars, namely, those which corresponded to the bottoms of the original ingots, it seemed unlikely that they were caused by the forging operation, but were present in the original ingots. Examination of the X-ray photographs showed that the abnormally high oxygen values were invariably associated with a shrinkage cavity of the type shown in Fig. 9, which, as indicated earlier, was believed to be due to too low a temperature during the cooling period after hydrogen treatment. Microscopical examination of sections just below the apparent termination of this type of cavity showed that it did in fact continue in the form of fine fissures, which, in the heating preliminary to forging, became oxidised and subsequently welded. From the point of view of producing bar with a uniformly low oxygen content, such ingots were very wasteful of time and labour, and care was accordingly taken to prevent the occurrence of this defect as far as possible.

The microstructure after forging varied somewhat from ingot to ingot, ranging from fine to medium in grain size. This variation probably depended upon the initial structures of the individual ingots. In general, the iron was still somewhat brittle and could not be cold-worked with certainty. Accordingly, the rolling operation was commenced with the bar and rolls hot.

The bar was first inspected for surface defects and filed smooth. It was then heated in an electric muffle at 620° C. and the bar rolls were raised to about 80° C. Starting at this temperature, rolling to

$\frac{1}{2}$ -in. round was accomplished with ease with no intermediate reheating. It was in fact noted that after a little further reduction in addition to that already given under the hammer, the iron suddenly became very ductile and that from this point any measure of cold-work could be applied. For example, some of this ductile material was cold-rolled to wire and thin foil.

For the present purpose, rolling was stopped when the bar was $\frac{1}{2}$ in. in dia. It was then straightened, cleaned with a fine file and inspected for imperfections. Owing to the low temperature used for rolling, the oxide layer was very thin and easily removed. For convenience, the bars were cut into shorter lengths, and oxygen determinations were made on both ends of every length. The results were remarkably consistent and of the order of 0.0005% of oxygen with a trace of nitrogen and hydrogen.

TABLE XXVIII.—*Oxygen Determinations on N.P.L. Iron, Mark 2.*

Bar No.	Laboratory and Method.	Oxygen. Weight-%.
9E	C.R.D.* Vacuum fusion.	0.0010
		0.0009
		0.0003
		0.0005
	N.P.L. Vacuum fusion.	0.0004
7E3	G.K.B. Aluminium reduction.	0.0006
	N.P.L. Vacuum fusion.	0.0006
12E4	G.K.B. Aluminium reduction.	0.0006
	N.P.L. Vacuum fusion.	0.0007

* These investigators remark that the variation in their results on specimens prepared at different times suggests that the oxygen is mainly present on the surface, and that it is significant that the lowest result was obtained on the specimen having the highest weight-to-surface ratio.

As pointed out earlier, evidence has now been obtained which suggests that this material is essentially free from internal oxygen, except for possible traces of unreduced alumina, and that the values represent surface oxygen the amount of which may vary slightly, depending upon the conditions prevailing during the preparation of the analytical specimen.

In other parts of Section III. of this Report references will be found to the uses which have already been made of this iron by Members of the Sub-Committee in investigating problems connected with the various methods of analysis for oxygen in steel. In addition, however, determinations of the actual oxygen content of the material have been carried out by the vacuum fusion method at The United Steel Companies, Ltd., Central Research Department and by the aluminium reduction method at Messrs. Guest Keen

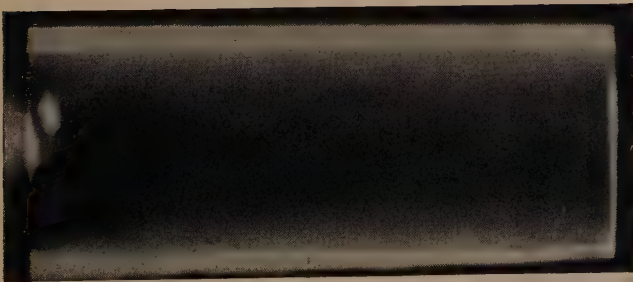


FIG. 7.—A Satisfactory Ingot.



FIG. 8.—Another Satisfactory Ingot.

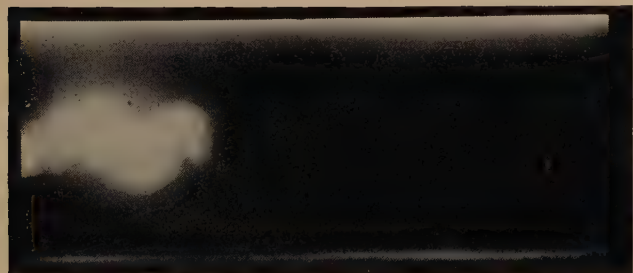


FIG. 9.—An Unsatisfactory Ingot. Compare the cavity with that in Fig. 8.

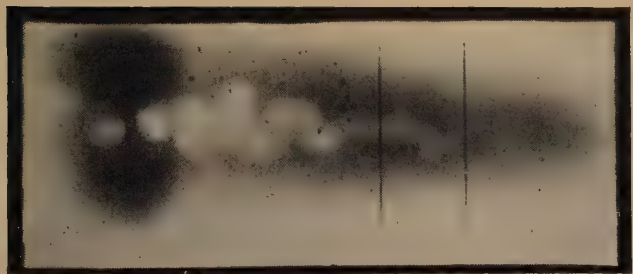


FIG. 10.—Type of Cavity resulting from uncontrolled cooling.

FIGS. 7 TO 10.—Radiographs of Ingots of Oxygen-Free Iron.

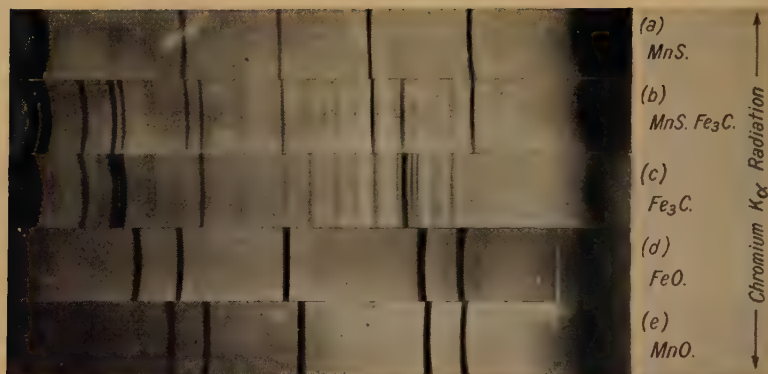


FIG. 11.—X-Ray Photographs. (a) and (b) Photographs of two residues from steel 1753MC; (c) to (e) standard photographs.



FIG. 12.—As Received



FIG. 13.—Heat-Treated at 1100° C.

FIGS. 12 and 13.—Steel 1753MC. Longitudinal section, unetched. $\times 2500$.

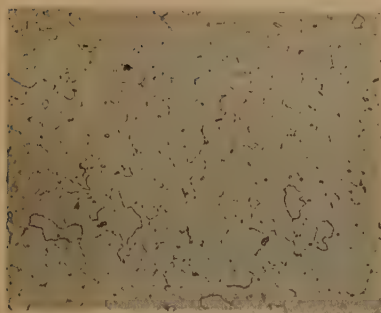


FIG. 14.—As Received.

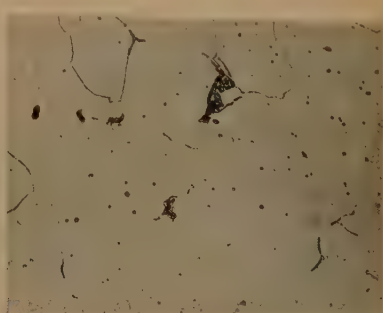


FIG. 15.—Heat-Treated at 1100° C.

FIGS. 14 and 15.—Steel 1753MC. Transverse section, etched in alcoholic nitric acid. $\times 150$.

(Micrographs reduced to four-fifths linear in reproduction.)

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Baldwins Iron and Steel Co., Ltd. The results together with those obtained at the National Physical Laboratory on the ends of the particular bars supplied to the above laboratories are given in Table XXVIII.

The work described above was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research for the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

(b) *THE SURFACE (OXYGEN) FILM ON IRON AND STEEL AND ITS EFFECT ON THE DETERMINATION OF OXYGEN.*¹

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SYNOPSIS.

A systematic study has been made of the surface oxygen on different types of specimens of iron and steel by the vacuum fusion and alcoholic iodine methods.

The results indicate that the amount of the surface oxygen on the disc-type specimen is not appreciably greater than that on the solid specimen.

The use of discs instead of solid specimens in the alcoholic iodine method does not seriously affect the results.

The oxygen content of the film on millings is, however, shown to be greater, in the majority of cases, than the internal oxygen of the steel itself and renders suspect any results obtained by their use.

Introduction.

Estimates of the thickness of very thin oxide films on iron and steel have been attempted by gravimetric, optical, spectrophotometric and electrochemical methods, and also by determining the ferric iron content of films stripped anodically. References to recent work by all these methods are given by Vernon, Wormwell and Nurse.²

These investigators attempted to strip the film chemically by means of the original method of Evans,³ who used a saturated solution of iodine in a 10% aqueous solution of potassium iodide to dislodge the film. In these experiments, the film was always contaminated, probably by hydroxide of iron precipitated from the solution. It became evident that, to avoid contamination, complete exclusion of both oxygen and water was necessary. This was rendered possible by substituting for the aqueous iodine solution the reagent employed by Rooney and Stapleton,⁴ viz., a solution of

¹ Received December 1, 1942.

² *Journal of the Chemical Society*, 1939, Apr., p. 621.

³ *Journal of the Chemical Society*, 1927, p. 1025.

⁴ *Journal of The Iron and Steel Institute*, 1935, No. I., p. 249.

iodine in anhydrous methyl alcohol. An important point is that the anhydrous iodine solution was de-aerated before use.

Using this solution, the values obtained for the oxygen content of the straw-coloured film on pure iron sheet were in good agreement with gravimetric determinations of the weight increment, but for the blue film the values by the stripping method were appreciably higher. These results indicated that with the blue film, when stripped, was incorporated some of the primary or air-formed film produced during the preparation of the specimen.

The amount of this air-formed film was determined by the vacuum fusion method,¹ but attempts to determine it by the stripping method yielded much lower values. The interesting point of these results to the Oxygen Sub-Committee is the inference that only a portion of the primary film, on both pure iron and mild steel, is recovered by the stripping method and that, therefore, a similar lack of recovery would occur in the determination of the primary oxide film on samples of these materials by the alcoholic iodine method, since the reagent and conditions are similar.

Thompson and Holm,² in work on the hydrogen reduction method for the determination of oxygen in steel, used a preliminary stripping process for the removal of surface oxygen on millings. This consisted of heating the millings to temperatures of up to 600° C. in a stream of hydrogen as recommended by Brower, Larsen and Shenk.³ It was felt that the values given by Thompson and Holm for the amount of the film on millings might be unduly high.

Meanwhile at the National Physical Laboratory it had been shown in experiments with the alcoholic iodine method⁴ on samples of pure iron that an increase in the oxygen values was obtained by the use of millings instead of thin discs, but with steels the increase was very much smaller. Nevertheless, the possible interference of surface oxygen led the operators of the method to advocate the use of discs instead of millings.⁵

The increase in the oxygen values for pure iron was, however, of a much lower order, for steels still lower, than would be inferred from the values for surface oxygen given by Thompson and Holm.

It was suggested that the pretreatment of the millings before use, as practised at the National Physical Laboratory,⁶ might account for part of the discrepancy in the values. The pretreatment, which consists of drying the millings in a stream of nitrogen

¹ Sloman, Second Report of the Oxygen Sub-Committee, Eighth Report of the Committee on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1939, *Special Report No. 25*, p. 43.

² National Bureau of Standards, 1938, *Research Paper No. 1114*.

³ *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1934, *Iron and Steel Division*, vol. 113, p. 61.

⁴ Rooney, Second Report of the Oxygen Sub-Committee, 1939, p. 146.

⁵ Rooney, Third Report of the Oxygen Sub-Committee, *Journal of the Iron and Steel Institute*, 1941, No. I., p. 344 P. Stevenson and Speight, *ibid.*, p. 352 P.

⁶ Rooney, *Journal of The Iron and Steel Institute*, 1924, No. II., p. 123.

or hydrogen immediately after preparation, removes moisture and prevents subsequent rusting. It is possible that the air-formed or primary film is unstable in character and may be partially removed by this treatment. Also, the oxygen in the primary film may combine with some of the phosphorus contained in a steel and therefore would not be included in the total oxygen value.

The evidence with regard to the rôle played by phosphorus is inconclusive, but it has been shown that the use of discs instead of millings combined with the deoxidation of the iodine solution considerably reduces the amount of P_2O_5 found in the residue.¹

By the vacuum fusion method it had been found that the film on pure iron sheet after rolling had an oxygen content corresponding to 0.6×10^{-6} g. per sq. cm., which rose to about 1.5×10^{-6} g. per sq. cm. after abrasion (Sloman, *loc. cit.*). Both these results are considerably lower than those which Thompson and Holm obtained with millings (10×10^{-6} g. per sq. cm.). This further supported the opinion that these investigators were in error, but, as will be seen from the present work, the effects of rolling and milling are not comparable.

The value of 0.6×10^{-6} g. per sq. cm. for the surface oxygen on the rolled sheet referred to above was derived from experiments in which a total oxygen of 0.0017% was obtained. Of this amount, 0.0014% represented the surface oxygen and 0.0003% the value given by a standard vacuum fusion specimen taken from the iron before rolling. Using somewhat thicker sheet of the same material, the alcoholic iodine method gave a total oxygen of 0.0018%, which appeared to be in good agreement with the vacuum fusion method and, in contradistinction to the stripping method of Vernon, Wormwell and Nurse (*loc. cit.*), suggested that the air-formed film on rolled sheet was recovered by the alcoholic iodine method. No determination was, however, carried out by this method on a solid specimen or on what, at the time, was assumed to be the same, namely, thin discs. The comparison between the vacuum fusion and alcoholic iodine methods was thus incomplete, and it was impossible to decide whether or not the apparent agreement on rolled sheet was fortuitous.

Working with a different sample of N.P.L. iron, on which the vacuum fusion method gave a value of 0.0012% of oxygen, a comparison was made between the use of discs and millings in the alcoholic iodine method. Here the former gave an average of 0.0014% of oxygen, which is in good agreement with the vacuum fusion method, while with the millings a value of 0.0073% of oxygen was obtained. The difference, 0.006% of oxygen, was presumably the surface oxygen on the millings and is equivalent to 2.4×10^{-6} g. per sq. cm. Once again the investigation was incomplete, since on this occasion the millings were not examined by the vacuum fusion method. However, at the time the value of 2.4×10^{-6} g. per sq. cm.

¹ Rooney, Second Report of the Oxygen Sub-Committee, 1939, p. 150, Table XLII.

obtained by the alcoholic iodine method on millings was compared with the value of 1.5×10^{-6} g. per sq. cm. (given above) obtained by the vacuum fusion method on abraded sheet, and was assumed to be in fair agreement. This once again suggested that the air-formed film was recovered by the alcoholic iodine method, but ignored the possibility of differences between millings and abraded rolled sheet.

It was in an attempt to clarify the position that the present more systematic investigation of the surface oxygen film on various types of specimen was undertaken. Determinations were carried out by both the vacuum fusion and the alcoholic iodine methods, on several different types of material in which the Oxygen Sub-Committee are interested. The actual materials used are listed below and have as far as possible been selected, as representative of a particular type, from among those upon which the Sub-Committee have already carried out investigations; the reference with each material is to the details of its manufacture and analysis:

- (1) N.P.L. iron, Mark 2. This Report, Section III.(a).
- (2) Iron-phosphorus alloy (0.05% phosphorus), EP05. (N.P.L. iron, Mark 2, and phosphorus).
- (3) Steel 1268, medium-carbon, high-phosphorus. Second Report of the Oxygen Sub-Committee, 1939, p. 201.
- (4) Steel 52703, low-carbon, aluminium-killed. Second Report of the Oxygen Sub-Committee, 1939, p. 204.
- (5) Cast iron, OP1. Second Report of the Oxygen Sub-Committee, 1939, p. 203.
- (6) Alloy steel (18% chromium, 8% nickel). This Report, Section III.(h).

Vacuum Fusion Method.

The investigation was planned to include the determination of the surface oxygen on millings and disc-type specimens of each of the above materials under various conditions. During the course of the work some modifications to the scope of the original plan became necessary but without materially affecting the deductions which can be drawn from the results.

It will be convenient to discuss the work on the two types of specimen separately.

Examination of Millings.

Preparation of Specimens.—The starting material in each case was a round bar of about $\frac{3}{8}$ in. dia. The requisite length was skimmed to a depth sufficient to remove all surface effects, and from the end a standard solid vacuum fusion specimen was cut. Up to 100 g. of millings were then taken, followed by a second solid specimen. The operation of preparing the millings was carried out in a closed cubicle, the temperature and humidity of which were approximately constant.

A small milling cutter with a standard feed and constant speed of rotation was used throughout. Figures are given later showing that the size of the millings obtained from the various materials differed widely. Immediately after preparation, the millings were placed in closed bottles. They were not touched by hand at any stage.

Capsule Containers.—In order to introduce the millings into the vacuum fusion apparatus and later into the reaction crucible, they were packed into containers. These capsules were prepared in the form of very thin-walled tubes, about 2.5 cm. long, 1 cm. in dia. and open at both ends. To close the ends, circular discs stamped from thin sheet were used. The design of stamp was arranged to produce appreciable convexity in the discs, so that with the convex surface uppermost a disc would drop through the capsule when held vertically in a clamping device. By the use of a hammer and a suitable flat-ended punch, the disc could again be flattened and thus expanded in position at the lower end of the capsule, so producing a very tight press fit. After filling the capsule with millings, it was closed by a similar disc, this one, however, being previously drilled with a series of small holes before stamping from sheet. These holes permitted evacuation of the container without loss of millings.

At the commencement of the investigation capsules were made by drilling pure iron rod (N.P.L. iron, Mark 2), but the wastage of material and labour involved led to a consideration of the possibility of obtaining and using commercially drawn thin-walled steel tubing of suitable diameter. Tubing of the stainless-steel type was finally selected, as it was found to have a comparatively low, consistent oxygen content (0.005%) and was very readily cleaned both internally and externally. The discs for the ends continued to be prepared from thin, pure iron sheet.

It was found that three or four such containers were required to hold 15–20 g. of millings, and this number was normally inserted into the reaction crucible at one time and treated as one specimen. Analyses were carried out from time to time on the empty capsules (with their end discs) to check the consistency in gas content. The gas content of the millings was obtained by deducting the blank for the capsules from the total gas evolved, while the surface oxygen was deduced by deducting the gas content of the solid specimens (assumed to be all internal, owing to the very small surface area) from the gas content of the millings.

Scope of the Investigation.—The millings were analysed under the following conditions :

- (1) Immediately after preparation :
 - A.—Without pretreatment.
 - B.—With pretreatment, described below.
- (2) After a few days.
- (3) After a few months.

As stated above, the millings were transferred to closed bottles immediately after preparation.

For (1A) above, the requisite number of cleaned, weighed capsules with one end already closed was prepared. They were filled with millings straight from the milling machine, closed with a perforated disc, reweighed, inserted in the vacuum fusion apparatus and evacuated as rapidly as possible. The solid specimens referred to above were analysed at the same time.

The pretreatment series (1B) was abandoned after a few preliminary experiments, as the pretreatment was found to have very little influence on the results. Where it was used, it consisted of

TABLE XXIX.—*Details of the Millings.*

Material.	Size of Milling.	Dimensions, Cm.			Surface Area per 100 g.* Sq. cm.	General Appearance of Millings.	Estimated Average Surface Area per 100 g. Sq. cm.
		Length.	Breadth.	Thick-ness.			
Pure iron (N.P.L. iron, Mark 2), EU3.	Coarse	0.60	0.20	0.10	430	Mostly coarse.	500
	Medium	0.20	0.10	0.10	640		
	Fine	0.10	0.07	0.07	990		
Iron-phosphorus alloy, EP05.	Coarse	0.45	0.15	0.10	485	Mostly medium.	600
	Medium	0.25	0.15	0.10	530		
	Fine	0.10	0.10	0.08	830		
Steel 1268 (medium-carbon, high phosphorus).	Coarse	0.45	0.20	0.10	440	Medium to fine.	1500
	Medium	0.25	0.15	0.04	910		
	Fine	0.10	0.07	0.02	1900		
Steel 52703 (low-carbon, aluminium-killed).	Coarse	0.25	0.10	0.07	725	Medium to coarse.	1000
	Medium	0.10	0.10	0.03	1370		
	Fine	0.08	0.05	0.03	1690		
Cast iron, OP1.	Coarse	0.25	0.10	0.05	870	Mostly fine. Much dust discarded.	1800
	Medium	0.15	0.06	0.04	1410		
	Fine	0.07	0.05	0.02	1980		
Alloy steel (18% Cr, 8% Ni).	Coarse	0.60	0.10	0.08	620	Medium to fine.	1300
	Medium	0.30	0.10	0.05	850		
	Fine	0.10	0.05	0.03	1620		

* A density of 7.8 has been assumed throughout.

passing a stream of dry, purified nitrogen over the millings (immediately after preparation) for several hours and then transferring them to the capsules and the apparatus as rapidly as possible.

For (2) and (3) the remainder of the millings was retained in the closed bottles for the requisite time and then analysed. After (2) had been completed, the bottles were opened for a few minutes once a week over the whole period of storage.

It should be noted that examinations at stages (2) and (3) were not carried out in every case, owing to pressure of other work. From the Table of results (Table XXX.) it will be seen that this does not materially affect the deductions which can be drawn from the investigation.

Size of Millings.—Table XXIX. shows the sizes of millings. In each case three sets of dimensions are given. They are representative of the coarse, medium and fine millings obtained from the particular material. Any pieces appreciably larger or smaller than the extreme dimensions given in the Table were discarded. The size of the pieces depends largely on the type of material; a mild steel tends to give large, a hard one small pieces. Experience has shown that it is not possible to obtain pieces all of one size by altering the speed or feed of the cutter.

If each piece is regarded as a rectangular parallelepiped, then its surface area and volume are readily calculated, and an approximate estimate of the surface area per 100 g. of material can be made. Such estimates are included in Table XXIX.

Results.—In addition to analyses for oxygen, determinations of nitrogen and hydrogen were also made in each case, and the complete results are given in Table XXX.

TABLE XXX.—*Gas Analysis on Millings.*

Material.	Type of Specimen.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.	
Pure iron (N.P.L. iron, Mark 2), EU3.	Solid	0.001 ₄	0.0010	Trace	
	Millings {	No pretreatment	0.024	0.0029	4.2
		Pretreatment	0.022	0.0031	4.0
		After 10 days	0.023	0.0029	4.3
		After 84 days	0.026	0.0028	4.8
Iron-phosphorus alloy, EP05.	Solid	0.003	0.0010	Trace	
	Millings—No pretreatment	0.022	0.0014	5.6	
Steel 1268.	Solid	0.013	0.0025	0.4	
	Millings {	No pretreatment	0.049	0.0026	4.1
		Pretreatment	0.048	0.0025	4.1
		After 10 days
		After 70 days	0.055	0.0025	6.6
Steel 52703.	Solid	0.003 ₄	0.0081	0.7	
	Millings {	No pretreatment	0.020	0.0079	3.8
		Pretreatment	0.020	0.0080	3.7
		After 10 days	0.025	0.0079	4.2
		After 67 days	0.024	0.0081	4.5
Cast iron, OP1.	Solid	0.002	0.0031	1.8	
	Millings {	No pretreatment	0.16	0.0072	40.9
		Pretreatment
		After 10 days
		After 81 days	0.41	0.0092	94.2
Alloy steel (18% Cr, 8% Ni).	Solid	0.017	0.012	1.8	
	Millings {	No pretreatment	0.031 ₁	0.010	2.2
		Pretreatment
		After 10 days
		After 81 days	0.034	0.011	2.3

Examination of Discs.

Preparation of Specimens.—The problem resolved itself into two parts: First, to obtain a specimen which could be readily manipulated in the vacuum fusion apparatus without recourse to capsules

and yet would closely approximate to the actual discs used in other methods, and secondly to obtain as large a surface area as possible in comparison with the standard cylindrical specimen of the vacuum fusion method. It was realised that, for a given weight, the surface area of discs would be considerably smaller than that of millings and that the differences in oxygen content which would be obtained would be correspondingly smaller. A higher degree of accuracy was therefore desirable and slight uncertainties introduced by the use of capsules, &c., must be avoided, if possible.

After various attempts to meet all the above requirements, a form of specimen was adopted which in practice proved very satisfactory. It should be noted that the discs normally used are obtained by sawing, and since the way in which the surface is produced is likely to have a large influence on the surface oxygen, the specimens used in these experiments should have sawn surfaces, although other methods of preparation would have been easier. A length of $\frac{3}{8}$ -in. bar was skimmed on the lathe as usual, and then with a fine saw a series of cuts, extending to within about 2 mm. of the centre, were made while the bar was very slowly rotated. The cuts were made at right angles to the axis of rotation and gave a specimen which was in effect a series of thin discs held together by thin connectors at the centre. The bar was parted off in 1-in. lengths, giving about 17 discs per inch weighing about 9 g., *i.e.*, about half the weight of a standard cylindrical specimen of the same length and diameter, and having about $2\frac{1}{2}$ times the surface area. For equivalent weights, therefore, the disc-type specimens had 5 times the surface area of the standard vacuum fusion specimens.

TABLE XXXI.—*Gas Analysis on Pure Iron (N.P.L. Iron, Mark 2).*

N.P.L. Pure Iron, Mark 2, 12E2.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.	Surface Area per 100 g Sq. cm.
Standard specimens.	0.00026	0.00018	Trace	60
Disc-type specimens.	0.00134	0.00019	0.6	327

The first material to be examined was the N.P.L. iron (Mark 2). The actual method of taking the specimens from a bar was as follows: After skimming to remove surface effects, one standard specimen was parted off. This was followed by 4 disc-type specimens and one more standard one. This cycle was repeated, giving 4 standard specimens and 8 disc-type ones in all. In this way, by treating the standard specimens as one, a reasonable volume of gas was obtained for analysis. Similarly the 8 disc-type specimens were also treated as one. After preparation, the total weight of the 4 standard cylinders was adjusted to be equal to that of the 8 disc-type specimens. The surface areas of the two types of specimen were calculated from their dimensions.

The results obtained are stated in Table XXXI. From these figures the surface oxygen due to the increased surface is :

$$\frac{0.00108}{267} \text{ g. per sq. cm.} = 4.0 \times 10^{-6} \text{ g. per sq. cm.}$$

At the commencement of this part of the investigation it was envisaged that experiments similar to that outlined above would be carried out on the other materials of the series examined in the form of millings. In this series, all the steels had considerably less surface oxygen in grammes per square centimetre than had the N.P.L. iron. It seemed probable that the same would apply for the disc-type specimens, and that the results would all be lower than that found above for N.P.L. iron, *i.e.*, <0.001%. In view of the internal oxygen contents of the steels, this very small additional surface oxygen would be extremely difficult to evaluate with accuracy, being within the limits of accuracy of the method itself. No further work has, therefore, been carried out.

Discussion of the Results.—The results obtained on the solid specimens taken from the bars immediately before and after the millings were consistent throughout, thus ensuring uniformity in the internal gas contents of the materials. From Table XXXI. it will be seen that the effect of the pretreatment of the millings after preparation is negligible, while storage, under the conditions specified, does not lead to an appreciable increase in gas content, except in the case of the cast iron, OPl.

In general, the nitrogen contents of the materials appear to be unaffected by the surface area of the specimens. This, however, is not true of the cast iron, nor, to a very much smaller extent, of the millings of pure iron. In these two cases it will be seen that, whereas the former shows a considerable increase in nitrogen on milling and a still further increase on storage, the latter, after a small initial rise, remains constant. It may be noted that the sawn disc-type specimens of pure iron do not show even this small increase in nitrogen (Table XXXI.), a result which was also noted in the earlier examination of rolled sheet of this material (Sloman, *loc. cit.*).

As regards oxygen, an appreciable increase was found in all cases as a result of milling. Ignoring the cast-iron sample for the moment, the increases are all of the same order when regarded as weight per cent. of oxygen, ranging from 0.014% in the case of the alloy steel to 0.036% in the case of steel 1268. On this basis the results are in general agreement with those of Thompson and Holm, who gave values ranging from 0.02% to 0.03% for the surface oxygen on a series of different steels.

When considering surface oxygen the weight percentage basis does not give so clear a picture as one based on weight of oxygen per unit area of surface. In Table XXXII. are given the values of surface oxygen per square centimetre of surface. Included also in the Table are the results for the disc-type specimens of pure iron and

those, previously published, for rolled sheet (*see* Sloman, *loc. cit.*), together with an average figure for Thompson and Holm's series of steels. It should be noted that these investigators state that the depth of cut was adjusted to give millings between 0.013 and 0.020 cm. in thickness for each steel. This gives an estimated surface area of about 2500 sq. cm. per 100 g., which was a constant for the whole series. The range of surface oxygen was from 0.02% to 0.03%, and in the Table a value of 0.025% has been used.

TABLE XXXII.—*Surface Oxygen Values per Unit Area.*

Material.	Surface Oxygen. Weight-%.	Estimated Average Surface Area per 100 g. Sq. cm.	Surface Oxygen per sq. cm. G. $\times 10^{-4}$.
Cast iron OP1	0.158 *	1800	89
N.P.L. iron, Mark 2	0.023 *	500	46
Iron-phosphorus alloy, EP05	0.019 *	600	32
Steel 1268	0.036 *	1500	24
Steel 52703	0.017 *	1000	17
Alloy steel (18% Cr, 8% Ni)	0.014 *	1300	11
Thompson & Holm's series of steels	0.025	2500	10
N.P.L. iron, Mark 2 (sawn discs)	0.0011	267	4
N.P.L. iron, Mark 2, sheet (rolled)	0.0014	2460	0.6
N.P.L. iron, Mark 2, sheet (rolled and abraded)	0.0038	2475	1.5

* Millings immediately after preparation with no pretreatment.

From Table XXXII. it will be seen that cold-rolling, sawing and milling lead to entirely different degrees of surface oxidation for the same material, *viz.*, pure iron, the increases in oxygen being in the ratio of 1 : 7 : 75.

If the results for the cast iron and the alloy steel, which Thompson and Holm did not investigate, are disregarded, the range of surface oxygen found in the present work for millings is 17×10^{-6} to 46×10^{-6} g. per sq. cm. (a ratio of about 1 : 2.7). This is in good agreement with Thompson and Holm's range of about 1 : 2 for their series of plain carbon steels and Armco iron, although the actual amounts are higher in the present work. (Thompson and Holm's range was about 7×10^{-6} to 15×10^{-6} g. per sq. cm.)

The surface oxidation resulting from milling probably depends on two factors: First, on the actual conditions of the operation. This will account for the absolute differences between Thompson and Holm's results and those obtained in the present investigation, referred to above. Second, on what may be called the "susceptibility" to oxidation of freshly cut surfaces of the various materials examined. For example, the susceptibility of the 18/8 alloy steel may be very different from that of the medium-carbon, high-phosphorus steel 1268, or again from that of the pure iron. This

type of difference is readily seen from Table XXXII., in which the materials used in the present work and all milled under the same conditions fall into a series of descending susceptibility.

It is interesting to note that while on a weight percentage basis the cast iron appears to differ entirely from the steels as regards surface oxygen, this difference tends to disappear when surface oxygen per unit area is considered. It would seem, however, that in the case of cast iron another possible factor may be introduced, namely, the adsorption of gas by the graphite exposed on the surfaces of the millings. Without postulating some such adsorption it is difficult to see why the increase in surface oxygen should be so large. The assumption is, moreover, borne out by the fact that large increases in nitrogen and hydrogen also occur and that all three show further increases on storage, in contradistinction to the other materials examined.

The results for hydrogen are extremely interesting. In every case an increase is found and it seems probable that this increase is associated with that of oxygen. The mechanism of surface oxidation would thus appear to be largely, if not entirely, one of reaction between the metal and water vapour, resulting in the formation of an oxide film and nascent hydrogen, the latter either entering the metal or remaining associated with the film, possibly as a hydroxide. The temperature attained during the operation of milling or sawing may be a factor in determining the extent of this reaction.

No very satisfactory relationship can be established between the increases in oxygen and hydrogen. Examination of the results given in Tables XXX. and XXXI. shows, however, that in every case except one the ratio of hydrogen to surface oxygen tends to be approximately constant. In the experiments with millings, this ratio for the carbon steels, pure iron and iron-phosphorus alloy is 0.02–0.04% of oxygen to 0.0003–0.0006% (3–6 ml. per 100 g.) of hydrogen. A similar ratio (0.001% of oxygen to 0.00006% (0.6 ml. per 100 g.) of hydrogen) is found for the sawn discs of pure iron and also for the cast iron (0.2% of oxygen to 0.004% (40 ml. per 100 g.) of hydrogen). The 18/8 alloy steel is outstanding in that the results show an abnormally small increase in hydrogen in comparison with the surface oxygen. Possibly the mechanism of oxidation is somewhat different for a stainless-type steel.

Considering now the results for sawn discs given in Table XXXI., an interesting relation appears if certain ratios are considered :

$$\frac{\text{Surface area of disc-type specimen per 100 g.}}{\text{Surface area of standard specimen per 100 g.}} = \frac{327}{60} = 5.45$$

and

$$\frac{\text{Total oxygen in disc-type specimen per 100 g.}}{\text{Total oxygen in standard specimen per 100 g.}} = \frac{0.00134}{0.00026} = 5.07.$$

This strongly suggests that the oxygen content of the N.P.L. iron is not internal but all, or practically all, on the surface, and that

its method of preparation does in fact result in the production of metal free from oxygen (e.g., the above results indicate that the internal oxygen is about 0.00002%).

The value of 4×10^{-6} g. per sq. cm. (see earlier) for the surface oxygen on pure iron discs represents the amount which must be added to the internal oxygen content in the case of specimens of pure iron having sawn surfaces. For the usual type of specimen consisting of about 20 discs (each 1 cm. in dia. and about 0.075 cm. in thickness) weighing 10 g., this corresponds to an additional 0.001% of oxygen, a value below which investigators should not be able to obtain results even on iron containing no internal oxygen unless some or all of the surface oxygen is not recovered. There can be no doubt that, just as with millings, the air-formed film on sawn surfaces results from the action of moist air on the freshly cut surfaces, as evidenced by the corresponding increase in hydrogen. It is possible, therefore, that this film is considerably less stable than the internal oxides and may not be fully recovered by some of the methods for determining oxygen.

By analogy with the results obtained on millings, the surface oxygen on disc-type specimens of steel should be less than on similar specimens of pure iron (i.e., <0.001% of oxygen). The differences due to the air-formed film between the results obtained with standard vacuum fusion and disc-type specimens will thus be very small and within the limits of accuracy of the various methods. Provided, therefore, that the surface-to-volume ratio of the two types of specimen is not more than 5 : 1, the use of discs is justified for the chemical methods where convenient, whether the small extra surface oxygen is recovered or not.

With millings, however, the oxygen content of the film (0.02% or 0.03%) is greater, in the majority of cases, than the internal oxygen of the steel itself, and renders any results obtained by their use very suspect.

Alcoholic Iodine Method.

Materials Examined.—The following materials were examined by the alcoholic iodine method :

- (1) N.P.L. iron, Mark 2.
- (2) Iron-phosphorus alloy (0.05% phosphorus), EP05.
- (3) Steel 1268 (medium-carbon, high-phosphorus).
- (4) Steel 52703 (low-carbon, aluminium-killed).

Examinations were carried out on discs and millings (pretreated) immediately after preparation.

The results, which are given in Table XXXIII., indicated that it would not be profitable to carry out the full programme as originally contemplated and set out earlier.

Discussion.—The results for total oxygen using the alcoholic iodine method on discs are in reasonably good agreement with those obtained by the vacuum fusion method using the standard specimen.

TABLE XXXIII.—*Oxygen Determination by the Alcoholic Iodine Method.*

	(1) N.P.L. Iron, Mark 2, EU3.		(2) Iron-Phosphorus Alloy EP05.		(3) Steel 1268.		(4) Steel 52703.	
	Discs.	Millings.	Discs.	Millings.	Discs.	Millings.	Discs.	Millings.
Total ignited residue.								
% :	0.0048	0.037	0.0067	0.027	0.065	0.080	0.017	0.023
SiO ₂ . % . . .	0.0009	0.001	0.0007	0.0009	0.010	0.012	0.001	0.001
FeO. % . . .	0.0031	0.029	0.0041	0.0205	0.005 _s	0.008	0.004	0.006 _s
Al ₂ O ₃ . % . . .	0.0005	0.0007	0.0032	0.0027	0.009 _s	0.011	0.009	0.013
MnO. %	0.011	0.008 _s	Trace	Trace
P ₂ O ₅ . %	Trace	0.0012	0.014 _s	0.029	0.001	0.001
Total oxygen, weight-% :								
Iodine method .	0.001 ₄	0.007 _s	0.003	0.006 _s	0.013	0.015	0.006	0.008
Vacuum fusion method .	0.001 ₂ *	0.022	0.003*	0.022*	0.013*	0.048	0.004*	0.020

* The vacuum fusion values in the columns headed "discs" refer to solid samples and were abstracted from Table XXX. All millings except those marked with an asterisk were pretreated.

The discs were about 0.75 mm. in thickness and averaged 20 discs per 10 g. sawn from the $\frac{3}{8}$ -in. rod which had been skimmed free from scale, &c.

Since, from Table XXXI., the discs should have a surface oxygen of 0.001% or less in addition to the internal oxygen, the conclusion is that very little of the air-formed film is recovered. Even if recovery were complete the error introduced would be very small and would only seriously affect materials of low oxygen content.

The air-formed film on millings is of a much higher order, and, in spite of incomplete recovery, it definitely vitiates the results, particularly on low-oxygen materials.

The results, therefore, confirm that the use of discs rather than millings is essential when employing the iodine method if reasonably accurate determinations are to be obtained.

The oxygen values recorded in Table XXXIII., column (1), have been obtained on a sample of iron containing appreciable amounts of total oxygen. When, however, irons substantially free from internal oxygen, *i.e.*, <0.001%, are examined, the iodine method tends to give results which are higher than those of the vacuum fusion method. The results are also somewhat erratic, indicating that the limits of accuracy of the present method and subsequent analytical procedure have been reached.

The limits of accuracy may be dependent on some of the following possible errors :

- (1) Residual traces of moisture or oxygen in the iodine solution.
- (2) Traces of oxygen in the nitrogen stream.
- (3) Variable recovery of surface oxygen.

To illustrate the effects of a small amount of extraneous oxygen due to any of the three causes above, assume that a very small amount—say, 0.07 ml.—of such oxygen is included in the residue on a 10-g. sample. This is equivalent to 0.001% of oxygen, and indicates the practical difficulties in attempting to obtain accurate results on materials substantially free from oxygen, *i.e.*, oxygen about 0.001%.

The work described above was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research for the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

(c) *THE EXAMINATION OF SEVERAL RIMMING STEELS BY THE ALCOHOLIC IODINE METHOD AND THE IDENTIFICATION OF CONSTITUENTS OF THE RESIDUE BY X-RAY METHODS.*¹

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(Under the direction of C. Sykes, D.Sc., F.R.S.)

(Figs. 11 to 15 = Plate XIX.)

SYNOPSIS.

In the Third Report of the Oxygen Sub-Committee an example was given of a modification to the standard iodine procedure which may be necessary for steels of the rimming type.

In the present work details are given of the examination of a number of rimming steels made by the acid Bessemer, basic open-hearth and basic Bessemer processes.

With all the samples except a low-carbon basic Bessemer steel the standard procedure gave satisfactory results. Even by the modified procedure, results on the low-carbon basic Bessemer steel were not satisfactory.

Details are given of the X-ray examination of unignited residues from several samples.

In an Appendix, by T. E. Rooney and H. A. Sloman, the determination of total oxygen in a residue by the vacuum fusion method is described and the result discussed.

Acid Bessemer Steel.

The first of the steels examined was made by the acid Bessemer process. No aluminium was used in the manufacture of this material. The pit-sample analysis was as follows: Carbon 0.17%;

¹ Received December 1, 1942.

manganese 0.285–0.325%; silicon 0.01–0.015%; nitrogen 0.0195–0.0205%; oxygen 0.022–0.0245%. For the examination $\frac{3}{8}$ -in. round bar was prepared which contained 0.013% of sulphur and 0.072% of phosphorus.¹

Vacuum Fusion Results.

Sample.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.
398/12	0.007	0.0165	0.1

An interesting point is the low total oxygen value obtained on the $\frac{3}{8}$ -in. bar as compared with that on the pit samples.

From information supplied by the Central Research Department of The United Steel Companies, Ltd., and Messrs. Stewarts and Lloyds, Ltd., this is not an unusual feature with rimming steels, but the difference in this case between the oxygen values on the pit sample and the $\frac{3}{8}$ -in. rod is very marked.

Alcoholic Iodine Results.

				Sample 398/12.			
				Standard Procedure.		Modified Procedure.	
Max. reaction temp. ° C.				65.5		31	
Total ignited residue. %				0.037		0.048	
SiO ₂ .	%	.	.	O ₂ .	%.	O ₂ .	%.
SiO ₂ .	%	.	.	0.0087	0.0046	0.0076	0.0040
FeO.	%	.	.	0.0101	0.0022	0.0094	0.0021
Al ₂ O ₃ .	%	.	.	0.0005	0.0002	0.0010	0.0005
MnO.	%	.	.	0.0091	0.0021	0.0188	0.0042
Cr ₂ O ₃ .	%	.	.	0.0007	...	0.0018	...
P ₂ O ₅ .	%	.	.	0.0046	...	0.0040	...
Total of constituents.	%	.	.	97.7	...	95.8	...
Total oxygen.	%	0.0091	...	0.0108

Basic Open-Hearth Steel.

A basic open-hearth rimming steel was examined next. The pit-sample analysis of this material was as follows: Carbon 0.22%; manganese 0.60%; silicon trace; sulphur 0.045%; phosphorus 0.021%.

Two lengths of $\frac{3}{8}$ -in. round bar were used. The sample marked 9273/1P had no aluminium addition but 9273/2P had an addition of 4 oz. of aluminium per ton during the teeming of the ingot.

Vacuum Fusion Results.

Sample.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.
9273/1P	0.013	0.0041	0.8
(No aluminium)	0.013	0.0040	0.9
9273/2P	0.012	0.0035	0.9
(Aluminium added)	0.012	0.0036	0.8

¹ In the preparation of specimens for vacuum fusion and alcoholic iodine determinations the $\frac{3}{8}$ -in. rod was skimmed in a lathe in order to remove the oxide scale.

Alcoholic Iodine Results.

		Standard Procedure.			
		9273/1P. No Aluminium.		9273/2P. Aluminium Added.	
Total ignited residue.	%	0.050		0.048	
		O ₂ %.		O ₂ %.	
SiO ₂ .	%	0.0096	0.0051	0.0093	0.0050
FeO.	%	0.0080	0.0018	0.0089	0.0020
Al ₂ O ₃ .	%	0.0056	0.0026	0.0056	0.0026
MnO.	%	0.0201	0.0045	0.0209	0.0047
Cr ₂ O ₃ .	%	Trace	...	Trace	...
P ₂ O ₅ .	%	0.0030	...	0.0017	...
Total of constituents.	%	98		101.5	
Total oxygen.	%	...	0.0140	...	0.0143

Basic Bessemer Steel.

Two examples of this type of rimming steel were examined, one containing 0.155% of carbon and the other 0.040%. The first sample was in the form of $\frac{3}{8}$ -in. rod and the analysis was as follows: Carbon 0.155%; manganese 0.55%; silicon trace; sulphur 0.040%; phosphorus 0.043%.

Vacuum Fusion Results.

Sample.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.
6972	0.005	0.013	Trace

Alcoholic Iodine Results.

		Standard Procedure. 6972.	
Total ignited residue.	%	0.027	
		O ₂ %.	
SiO ₂ .	%	0.0020	0.0011
FeO.	%	0.0073	0.0016
Al ₂ O ₃ .	%	0.0008	0.0004
MnO.	%	0.0098	0.0022
Cr ₂ O ₃ .	%	0.0009	...
P ₂ O ₅ .	%	0.0039	...
Total of constituents.	%	98.6	...
Total oxygen.	%	...	0.0053

The experiments, recorded above, on three rimming steels indicate that the standard iodine method ¹ gives satisfactory results. The modified procedure used on steel 398/12 differs from the standard only in that no external heat is applied to the reaction vessel and the maximum temperature reached was 31° C.

Low-Carbon Basic Bessemer Steel.

The analysis of this steel was as follows: Carbon 0.04%; manganese 0.41%; silicon <0.005%; sulphur 0.047%; phosphorus 0.041%.

¹ Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 345 P.

Two samples of this cast of steel were examined in the form of $\frac{3}{8}$ -in. rod. One bar, 1753MB, was from an ingot to which 1.8 oz. of aluminium per ton was added and the other bar, 1753MC, was from an ingot to which no aluminium was added.

Vacuum Fusion Results.

Sample.	Oxygen. Weight-%.	Nitrogen. Weight-%.	Hydrogen. Ml. per 100 g.
1753MB as received	0.020	0.021	Trace
1753MC as received	0.027	0.014	1.0

Alcoholic Iodine Results.

The results obtained by the alcoholic iodine method are recorded in Table XXXIV. Both samples yield low values for total oxygen by

TABLE XXXIV.—*Alcoholic Iodine Results on Steels 1753MB and 1753MC.*

	1753MB. Aluminium added. As received.		1753MC No Aluminium added. As received.	
	Standard Procedure.	Modified Procedure.	Standard Procedure.	Modified Procedure.
Max. reaction temp. °C.	65.5	33	65.5	35
Total ignited residue. %	0.046	0.101	0.036	0.088
	O ₂ . %.	O ₂ . %.	O ₂ . %.	O ₂ . %.
SiO ₂ . %	0.0007	0.0004	0.0006	0.0003
FeO. %	0.0079	0.0017	0.0050	0.0011
Al ₂ O ₃ . %	0.0026	0.0012	0.0015	0.0007
MnO. %	0.0302	0.0068	0.0232	0.0052
Cr ₂ O ₃ . %	0.0015	...	0.0015	...
P ₂ O ₅ . %	0.0018	...	0.0009	...
Total of constituents. %	103.8	100	99.0	100
Total oxygen. %	...	0.010	...	0.007
		0.021		0.018

the standard procedure as compared with the vacuum fusion method. Also, higher values for total oxygen are obtained by the modified procedure, but in the case of sample 1753MC the value was still considerably less than that obtained by vacuum fusion. Subsequent work, which will be referred to later, indicated that the higher values obtained with the modified treatment can be largely attributed to the presence of manganese sulphide in the residue before ignition.

The low results by the standard procedure may be due to the solubility of very fine particles of iron and manganese oxide in the hot iodine solution. An attempt was made to cause an aggregation of the inclusions by suitable heat treatment.

The results on these heat-treated samples are given in Table XXXV. The total oxygen was also determined by the vacuum fusion method.

TABLE XXXV.—*Oxygen Determination on Heat-Treated Samples of Steel 1753MC.*

Method:	Modified Procedure.					Standard Procedure.
	(1)	(2)	(3)	(4)	(5)	(6)
Heat treatment:	600° C. for $\frac{1}{2}$ hr., Slowly Cooled.	750° C. for $\frac{1}{2}$ hr., Slowly Cooled.	950° C. for $\frac{1}{2}$ hr., Slowly Cooled.	750° C. for $\frac{1}{2}$ hr., Slowly Cooled, 750° C. for $\frac{1}{2}$ hr., Cooled in Air.	1100° C. for 1 hr., 600° C. for 16 hr., Slowly Cooled.	
Max. reaction temp. ° C. . . .	34	36	31	29	31	65.5
Total ignited residue. % . . .	0-0102	0-0106	0-0109	0-112	Residue very coarse before ignition. 0-185	Residue fine before ignition. 0-028
SiO ₂ . %	0-0009	0-0008	0-0008	0-0008	0-0010	0-0010
FeO. %	0-0275	0-0395	0-0211	0-0135	0-0869	0-0045
Al ₂ O ₃ . %	0-0002	0-0009	0-0008	Trace	0-0011
MnO. %	0-0602	0-0542	0-0810	0-0882	0-0760	0-0005
Cr ₂ O ₃ . %	0-0015	0-0015	0-0016	0-0016	0-0171	0-0040
P ₂ O ₅ . %	0-0015	0-0014	...
Total of constituents. % . . .	97.0	100	105	102	98	103.5
Total oxygen by—						
Iodine method	0-020	0-022	0-037	0-006
Vacuum fusion	0-027	0-027	0-024	0-024	0-028	0-028

The main effect of the heat treatment in all cases except one was to increase the total oxygen value as determined by the modified iodine procedure, but the highest value obtained (0.024%) was still below the vacuum fusion value (0.027%). The exception was the sample heat-treated at 1100° C. for 1 hr., cooled at 100° per hr. to 600° C., held at 600° for 16 hr. and cooled to room temperature in about 3 hr. By the modified procedure this sample gave an oxygen value of 0.037%, but by the standard procedure the value was 0.006%, very similar to that obtained by the same method on the sample as received (Table XXXIV.). The high value by the modified procedure suggested that the residue contained iron and manganese in some form other than oxide. The residue, before ignition, was very coarse and relatively small in bulk, and as the carbon content of the steel was low (0.04%) it seemed that an X-ray examination might indicate whether any oxide of iron or manganese was present.

X-Ray Examination of Residues.

Previous work at the National Physical Laboratory on the X-ray examination of unignited residues gave negative results.¹ It was considered possible that the effect of the small amount of mineral matter present might be masked by the relatively much larger amount of carbon in the residue. The steels examined contained 0.16% and 0.44% of carbon. When the carbon was removed by a low-temperature ignition the results were again negative. Faint lines possibly due to α ferric oxide were obtained after ignition at about 1000° C.

A similar result was reported by Jay and Stevenson² on carbon steels, but a series of very low-carbon (0.02%) steels containing preponderating amounts of oxide constituents gave much more promising results.

As noted above, it was considered that by an X-ray examination of an unignited residue from steel 1753MC, heat-treated at 1100° C., it might be possible to identify some of the constituents.

An X-ray examination³ did reveal the presence of appreciable quantities of manganese sulphide, MnS, and iron carbide, Fe₃C. The constituents in the residue were identified by comparison of the photographs with those of standard substances taken under similar conditions.

In consequence of the result recorded above, X-ray examinations were made on other residues from steels 1753MB, 1753MC and 6972 (basic Bessemer, carbon 0.16%) and on a residue from a low-carbon rimming steel (carbon 0.04%) included in the Third Report (see p. 346 P).

¹ Second Report of the Oxygen Sub-Committee, *Iron and Steel Institute*, 1939, *Special Report No. 25*, Section VI., pp. 151–153.

² Second Report, p. 195.

³ All X-ray photographs in this report were taken in a 9-cm. dia. Debye-Scherrer camera, using chromium radiation.

Fig. 11 (a) and (b) shows photographs of two residues from steel 1753MC; (a) (see Table XXXVI., column 3) shows only MnS, whilst (b) (Table XXXVI., column 5) shows both MnS and Fe_3C ; a standard photograph of the latter is given in Fig. 11 (c).

Comparison with standard photographs of FeO (d) and MnO (e) showed that there was no visible trace of either of these compounds in the photographs of the two residues. All the X-ray results, together with oxygen values, are summarised in Table XXXVI.

TABLE XXXVI.—X-Ray Results and Corrected Oxygen Values.

Steel No. :	(1) 1753MB.	(2) 1753MC.	(3) 1753MC.	(4) 1753MC.	(5) 1753MC.	(6) Third Report, p. 52.
Heat treatment :	As received.	As received.	As received.	1 hr. 1100°, 16 hr. 600° C.	1 hr. 1100°, 16 hr. 600° C.	As received.
Iodine procedure :	Standard, 65.5° C.	Standard, 65.5° C.	Modified, 35° C.	Standard, 65.5° C.	Modified, 33° C.	Modified, 33° C.
X-ray examination	MnS.*	MnS faint, MnO very faint.	MnS.	MnS.*	MnS, Fe_3O_4 .	MnS, Fe_3C very faint.
Chemical estimation of MnS. %	0.014 _s	0.006	0.033	0.015	0.025	0.024
Total oxygen, Tables XXXIV. and XXXV. %	0.010	0.007	0.018	... †	0.037	0.024 _s
Oxygen equivalent of MnS. %	0.002	0.001	0.006	...	0.022 ‡	0.004 _s
Corrected total oxygen. %	0.008	0.006	0.012	...	0.015	0.020

* Some very faint extra lines, which were not identified, were also present on these photographs.

† The residue used for X-ray examination and MnS determination was greater in amount and coarser in texture than that used for the full analysis (Table XXXV.) and probably contained much less MnS. It was, therefore, not possible to obtain a corrected value.

‡ Also corrected for Fe_3O_4 .

In addition to the X-ray investigation, manganese sulphide and cementite were determined by other methods in residues from the steels mentioned in Table XXXVI. and steels 398/12 and 9273/1P.

Manganese sulphide in the residues was determined by an evolution method. The residue was treated with hydrochloric acid and the sulphuretted hydrogen evolved was absorbed in cadmium acetate solution. The cadmium sulphide formed was titrated with standard iodine and sodium thiosulphate solutions.

Iron carbide, Fe_3C , when present in appreciable amount, was separated from the residue by magnetic means. A carbon determination on the magnetic portion indicated an excess of carbon above that required to form Fe_3C . The iron content was therefore estimated and calculated to Fe_3C . If iron is present in forms other than carbide the value so obtained may be too high.

The X-ray examination on steel 6972 revealed no MnS; similarly chemical analysis indicated that MnS was absent from steels 6972, 398/12 and 9273/1P.

The corrected oxygen values in Table XXXVI. were obtained by deducting the oxygen equivalent of the MnS chemically determined on the residues used for X-ray examination from the oxygen values recorded in Tables XXXIV. and XXXV. obtained by the full analysis of similar residues.

These values should be regarded as only approximate. However, they do indicate that the use of the modified treatment effects little, if any, improvement and, on the other hand, especially when combined with heat treatment, may lead to an artificially high oxygen figure due to the presence of undecomposed MnS and Fe_3C .

It will be noted, in steels 1753MB and 1753MC, that manganese sulphide is retained in all the residues, irrespective of the iodine procedure or the heat treatment. A surprising feature is the presence of MnS in residues prepared by the standard procedure, but a greater amount is retained in residues prepared by the modified treatment.

These results led to the examination, as recorded above, of residues prepared by the standard procedure from other rimming steels and, in particular, of a residue obtained by the modified procedure from a low-carbon rimming steel, the results of which are given in the last column of Table XXXVI. Some manganese sulphide and a faint indication of iron carbide, Fe_3C , were found in the latter residue and the corrected value for total oxygen is equal to the vacuum fusion value of 0.020%. Oxide was not detected by the X-ray examination. A faint trace of MnO was found in one residue corresponding to 0.006% of total oxygen in the steel. It seems that any oxide present was in a form not easily detected by X-ray examination.

In order to confirm that oxide is actually present in an unignited residue, a determination was made by the vacuum fusion method; a value of 0.009% of oxygen was found. The method is described and the result discussed in the Appendix which follows.

Microscopical Examination.

Longitudinal sections of 1753MC, as received and after the 1100° C. heat treatment, were examined in the polished but unetched condition. The form and number of inclusions in each section appear to be similar. Many of the inclusions are duplex, and probably consist of oxide and sulphide, Figs. 12 and 13.

Transverse sections of the two specimens, polished and etched, are shown in Figs. 14 and 15. The carbide in the specimen as received, Fig. 14, is present as thin films in the grain boundaries and is not readily discernible at the magnification shown. In the heat-treated specimen the carbide is for the most part present as spheroidised pearlite, although there are some carbide films in the grain boundaries, Fig. 15. The ferrite grains of the heat-treated specimen are much coarser than the grains of the bar in the condition as received.

Summary.

(1) Satisfactory results have been obtained on three rimming steels by the standard alcoholic iodine method. All three steels contained over 0.15% of carbon.

(2) A residue prepared by the modified procedure from a low-carbon rimming steel contained some manganese sulphide, but the corrected value for total oxygen was in agreement with the vacuum fusion value.

(3) Results by both the standard and the modified procedure on two samples of basic Bessemer steel (carbon 0.04%) were low and the residues contained manganese sulphide.

(4) Heat treatment of the steel produced a tendency, sometimes very marked, for the retention of cementite in residues obtained by the modified procedure. Residues from such types of steel should therefore be examined for manganese sulphide and cementite.

The work described above was carried out in the Metallurgy Department of the National Physical Laboratory as part of the programme of research for the Oxygen Sub-Committee, and this paper is published by permission of the Director of the Laboratory.

Appendix.—The Determination of Total Oxygen by Vacuum Fusion on a Residue Prepared by the Alcoholic Iodine Method.

By T. E. ROONEY, A.M.S.T., F.I.C., AND H. A. SLOMAN, M.A.
(Under the direction of C. Sykes, D.Sc., F.R.S.)

Sample.

The basic Bessemer steel 1753MC was chosen for this experiment. It was heat-treated at 1100° C. for 1 hr., at 600° C. for 16 hr. and slowly cooled. This sample was chosen because the residue on previous determinations was coarse and not bulky, and the low carbon content reduced the risk of absorption of oxygen during transfer from the filter to a capsule for the vacuum fusion determination.

Preparation of the Residue and Transfer to a Capsule.

The residue was prepared by the modified procedure, i.e., the temperature during the reaction did not exceed 30° C. It was filtered on a "Cella" filter, the smooth surface of which facilitated the washing-off of the residue for transfer to a capsule. The residue was washed free from iodine solution with oxygen-free alcohol in the usual manner, but an atmosphere of pure nitrogen was maintained over the filter until the end of the operation. The filter was detached from the flanges of the apparatus, trimmed and immersed in oxygen-free benzene. The small amount of residue adhering to

the top flange was washed into the benzene vessel by means of a small wash flask. The filter was brushed with a small camel-hair brush, washed free from residue and removed.

The benzene containing the residue in suspension was poured into a glass tube to the bottom end of which a (pure-iron) capsule was fixed. The tube and attached capsule were centrifuged, and the clear benzene was poured off. The remnants of residue in the benzene vessel were washed into the tube, which was again centrifuged. The finer portions of the residue settled rather sluggishly and the tube was allowed to stand overnight.

In the morning the tube was again centrifuged and the benzene was poured off. It still contained some very fine particles in suspension, which were dealt with later.

The capsule containing the residue together with a small amount of benzene was detached from the glass tube, carefully wiped outside, closed with a perforated disc and placed in a small glass bottle, which was closed with a stopper. The stopper carried an exit tube closed with a two-way tap. The bottle was exhausted three times and oxygen-free nitrogen was admitted after each exhaustion. This process removed practically all the benzene. The capsule in an atmosphere of nitrogen was then ready for transfer to the vacuum fusion apparatus.

Small amounts of residue which for various reasons could not be transferred to the capsule, including the fine particles suspended in the benzene (noted above), were collected together. Iron and manganese were determined, and it was calculated from previous determinations that the amount of residue not transferred to the capsule was approximately one-third of the total.

Vacuum Fusion Determination.

The capsule was made from N.P.L. iron, Mark 2, bar and the closing disc from thin sheet of the same material. In order to allow for the blank due to the capsule with its lid, an exactly similar but empty one was analysed for oxygen, hydrogen and nitrogen during the same experiment as the one containing the alcoholic iodine residue.

The vacuum fusion apparatus was set up ready for preliminary evacuation with some specimens of iron (N.P.L., Mark 2) in the specimen carrying tube for use as a bath.

The capsule containing the residue was removed from the closed bottle and, together with the empty capsule, placed in the specimen tube and the apparatus immediately evacuated. In order to ensure that all the residual benzene was removed, the apparatus was continuously evacuated for 24 hr. before the actual determinations were carried out. The results, after allowing for the blank due to the capsule, were :

Oxygen.	Nitrogen.	Hydrogen.
0.007%	0.005%	Trace

The absence of hydrogen suggests that no benzene was retained by the residue, while the oxygen value indicates that the method of transferring the residue from the alcoholic iodine to the vacuum fusion apparatus was satisfactory in preventing the absorption of oxygen. The method might, however, not be so completely successful if the experiment were carried out on a steel containing higher carbon.

The presence of nitrogen is capable of two explanations. Either it was absorbed by the residue on drying in an atmosphere of nitrogen or else it was present as nitride not completely decomposed by the original iodine treatment (the steel used contained 0.014% of nitrogen).

Assuming that the one-third portion of the total residue which was not transferred to the capsule contained the same proportion of oxygen, a correction should be made of about +0.002% of oxygen to the vacuum fusion value, giving a total of 0.009%.

Comments on the Result.

The final result for oxygen of 0.009% may be compared with the value of 0.015% obtained on a similar sample by the usual method of analysis corrected for MnS and Fe₃C (Table XXXVI., col. 5). The difference is rather large and possible explanations are :

(1) The recovery of oxide on this particular steel after heat treatment may vary in successive iodine separations. The residue in this instance was not as coarse as and was more bulky than the similar one referred to above, and it did not appear to contain any cementite (magnetic test).

(2) A larger proportion of oxide may be retained in that part of the residue (finer portion) which was not included in the vacuum fusion determination.

Also some of the residue may have been lost in the more elaborate technique involved.

Conclusion.

The above experiments lead to the conclusion that some oxide is retained in the residue and the oxygen content actually estimated is of the same order as that recorded in Table XXXVI., viz., 0.006-0.015% of oxygen. This amount is much less than that contained in the steel (0.027%).

(d) *THE GAS CONTENT OF THE RAW MATERIALS USED IN STEELMAKING.*¹

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SYNOPSIS.

Results obtained for the gas content of the raw materials used in steelmaking are published and commented upon. Considerable variation exists between different samples, and under each material considered a series of actual results obtained is stated, so that not only the order of magnitude of the oxygen, hydrogen and nitrogen contents found but also the likely range of variation may be seen. The significance of the gas content of these materials is considered.

In this paper is given a series of typical results, collected over a period of several years, for the gas contents of commercial materials in the condition in which they were about to be added to steel-melting baths. Discretion and discrimination were exercised in the selection and preparation of the small samples suitable for examination, and the guiding principle was that the sample taken and prepared should be representative of the whole quantity of the material being added. In accord with that principle the samples were not cleaned, and were taken in the form of a number of small pieces, or were broken from a larger piece, in such a manner that the proportion of outside surface was as nearly as could be estimated the same as that of the whole mass of material. Heterogeneity is marked in such raw materials, and it is for this reason that the results have been stated to fewer significant figures than is usual for homogeneous products. Likewise, the general analytical figures have been rounded off, so that unjustified assumptions should not be made. It is for this reason also that individual results have been given in preference to averages, and several examples are given of the possible variations which occur from specimen to specimen and from sample to sample.

Whilst it is often considered that from the steel-melting standpoint the quality of these raw materials is connected with their gas content, very little has been published on the subject. Siegel² gives details of a fusibility test applied by means of a blow-torch to certain of the minor ferro-alloys, and compares their behaviour in this test with their gas content and their behaviour in the steel-melting bath. His figures show correlations, and he suggests that the blow-torch test could be used for the rough classification of the gas content and quality of those ferro-alloys. The authors are glad that more recently the National Physical Laboratory has commenced the systematic examination of the gas content of steel-

¹ Received March 9, 1943.

² *Stahl und Eisen*, 1940, vol. 60, pp. 1125-1131.

making raw materials, and they acknowledge the privilege of being able to publish the National Physical Laboratory results together with a few results from the Central Research Department of The United Steel Companies, Ltd. Representative figures from these two laboratories have been inserted in the Tables of figures below, so that the gas content of raw materials from as many different sources as possible may be considered.

The method used for the determinations has been the vacuum fusion method as described in earlier Reports of the Heterogeneity of Steel Ingots Committee, except for the high-nitrogen ferrochromes, which are more satisfactorily examined by the chemical method for nitrogen, owing to the large volume of that gas evolved by vacuum fusion. Several of the nitrogen figures for other raw materials have been substantially confirmed by the chemical method, and a few of the hydrogen figures have been confirmed by the vacuum-heating method.

The Gas Content of Commercial Nickel (Table XXXVII.).

Nickel is supplied in the form of small shot prepared by the Mond carbonyl process, and in the form of about 4-in. square plates

TABLE XXXVII.—*Gas Contents of Commercial Nickel.*

Condition.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Shot:					
Stock A, after long storage . . .	B.F.R.L.	0.027	0.0015	17	0.003
Stock B, newly received . . .	B.F.R.L.	0.020	0.0083	93	0.001
Stock C, newly received . . .	N.P.L.	0.008	0.0017	19	...
Stock D, newly received . . .	B.F.R.L.	0.060	0.0076	85	0.006
Do. after $\frac{1}{2}$ hr. at 650° C. in air	B.F.R.L.	0.048	0.0014	16	0.007
Do. after 1 hr. at 850° C. in air	B.F.R.L.	0.151	0.0002	2	0.009
Stock D, another sample . . .	B.F.R.L.	0.021	0.0022	24	<0.0005
Cathode:					
Stock E, after long storage . . .	B.F.R.L.	0.008	<0.00005	<0.5	0.004
Stock F, newly received . . .	B.F.R.L.	0.011	0.0010	11	0.002
Thin	B.F.R.L.	0.014	0.0015	17	0.001
Medium thick } from stock G	B.F.R.L.	0.002	0.0001	1	0.001
Thick	B.F.R.L.	0.002	0.0002	2	<0.0005
With few "warts"	B.F.R.L.	0.003	0.0005	5.5	0.001
Do. after 1 hr. at 850° C. } from	B.F.R.L.	0.024	<0.00005	<0.5	0.003
With many "warts" } stock H	B.F.R.L.	0.009	0.0001	1	<0.0005
Do. after 1 hr. at 850° C. }	B.F.R.L.	0.071	<0.00005	<0.5	0.003

prepared electrolytically and hence generally designated "cathode nickel." Both are very pure materials from the commercial standpoint, the shot usually containing about 99.8% of nickel, 0.15% of iron and 0.05% of carbon, and the cathode metal about 99.5% of nickel and 0.5% of cobalt. Though the oxygen and nitrogen contents of commercial nickel are low, the hydrogen content can be quite high—a fact which is not surprising in view of the high solubility

of hydrogen in nickel. It has been found that in the course of time hydrogen diffuses out of nickel, so that stocks which have been kept for a period of several months have a very much lower hydrogen content than that of freshly produced metal. The loss of hydrogen can be hastened by heating in air, as the figures in Table XXXVII. show. It is of interest to note that the heat treatment at 650° C. has resulted in a loss of oxygen as well as of hydrogen. This is presumably due to reduction of oxide by the liberated hydrogen, and is confirmed by the visible brightening of the nickel by this treatment. At 850° C. atmospheric oxidation prevailed and the sample tarnished and increased in oxygen. The deposition of nickel electrolytically does not always take place uniformly, with the result that the cathode material may have local areas of apparently excessive deposition with an appearance resembling warts. This phenomenon appears to bear some relationship to the gas content of the metal.

Cobalt and Rhokana Alloy (Table XXXVIII.).

Cobalt metal is usually supplied in small cylindrical pieces, having a clean bright appearance. The metal is a sintered product of the reduction of the oxide, and can easily be crushed and crumbled into small fragments. Internal surfaces after fracture are rough and dull, contrasting sharply with the smooth, bright external

TABLE XXXVIII.—*Gas Contents of Cobalt and Rhokana Alloy.*

Type of Cobalt or Alloy.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
99% Co	B.F.R.L.	0.22	0.0047	53	0.019
97% Co	N.P.L.	0.070	0.0017	19	0.008
Rhokana alloy, 38% Co, 16% Cu, 1% S, 0.02% C	N.P.L.	0.52	0.004	45	0.042

surface, and are often coloured as though in an oxidised condition. As would be expected from the nature of the product, the oxygen content can be very high, as can also the hydrogen content. Rhokana alloy is a cobalt-copper alloy which is sometimes used for steels containing both cobalt and copper. Its gas content is also very high.

Aluminium (Table XXXIX.).

The type of aluminium used in steel manufacture depends upon whether it is employed merely as a deoxidant or as an essential constituent of the steel being made. For deoxidation purposes, since such a small proportion is added to the steel, remelted aluminium and alloyed aluminium can be utilised, but where the aluminium is to remain as an essential constituent of the steel

virgin metal of at least 99% purity is to be preferred. From the point of view of gas content, aluminium is almost invariably low.

TABLE XXXIX.—*Gas Contents of Aluminium.*

Type of Aluminium.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Virgin	B.F.R.L.	0.001	0.00015	1.5	0.001
Remelted, 95%	B.F.R.L.	0.002	0.00030	3.0	0.0005

Aluminium oxide does not appear to be soluble in the metal, and the solubility of both hydrogen and nitrogen is very low. Since aluminium is a metal which easily forms a nitride, it is surprising that it normally contains so small an amount of nitrogen. The possibility of an aluminium nitride, stable at high temperatures and incompletely dissociating *in vacuo*, has been considered, but as yet no evidence of larger amounts of nitrogen has been obtained by the acid-hydrolysis or chemical method, or by alkali-hydrolysis.

The volatility of aluminium is such that if a sample is inserted into an empty crucible at 1600° C. (the usual vacuum-extraction temperature), then the metal is rapidly distilled off to cooler portions of the furnace. The hydrogen content of aluminium can be determined by heating *in vacuo*, provided that the temperature is high enough to melt the metal. To effect the reduction of aluminium oxide a very much higher temperature is necessary, and the most satisfactory way of quantitatively reducing the oxide and of minimising the volatility of the metal is to insert the aluminium sample into a bath of molten iron, many times the weight of the aluminium, contained in a carbon crucible at 1600° C.

Pig Iron (Table XL).

On the basis of physico-chemical theory one would expect a high-carbon material such as pig iron to be low in oxygen. Usually

TABLE XL.—*Gas Contents of Pig Iron.*

Type and Condition of Iron.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Swedish white	B.F.R.L.	0.020	0.0047	52	0.003
Hematite	B.F.R.L.	0.006	0.0005	5	0.003
Hematite, 1% Mn	B.F.R.L.	0.006	0.0005	5	0.003
Hematite	N.P.L.	0.011	0.0004	4	0.005
After remelting	B.F.R.L.	0.003	0.00015	1.5	0.002
Phosphoric hematite	N.P.L.	0.008	0.0005	6	0.004
After remelting	B.F.R.L.	0.004	0.0003	3	0.001

this is so, and for samples which are high in oxygen it is reasonable to assume that the oxidic inclusions are foreign. Confirmation of this is obtained from the fact that the simple remelting of a high-oxygen sample under controlled conditions does result in the oxygen content being brought down to the usual low order of magnitude.

It is noteworthy that Swedish iron is substantially higher in oxygen and hydrogen than the hematite irons of Great Britain.

Scrap Steel (Table XLI.).

Since steel scrap is one of the major constituents of the charge of a steel-melting bath, it is desirable that we should know the magnitude of the quantities of gas present in such additions. The nature of the scrap and the oxidation, hydration and contamination that it undergoes before it is back again on the furnace stage largely determine its gas content, which is as a rule much higher than that

TABLE XLI.—*Gas Contents of Scrap Steel.*

Type of Scrap Steel.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Mild steel	N.P.L.	0.012	0.0001	1	0.004
Bought, assorted carbon	B.F.R.L.	0.21	0.0031	35	0.003
Carbon, springs	B.F.R.L.	0.099	0.0038	42	0.010
Carbon, forged bar	B.F.R.L.	0.004	0.0001	1	0.001
Bought, carbon sheet	B.F.R.L.	0.13	0.0003	3	0.002
Ni-Cr, billet crops	B.F.R.L.	0.007	0.0047	52	0.008
Ni-Cr, turnings	B.F.R.L.	0.032	0.0014	16	0.003
Ni-Cr, 5-in. round	B.F.R.L.	0.003	< 0.00005	< 0.5	0.008
Ni-Cr, 5-in. square	B.F.R.L.	0.007	< 0.00005	< 0.5	0.006
Ni-Cr-Mo, turnings	B.F.R.L.	0.030	0.0017	19	0.003

of clean solid metal. A fact which reduces the importance of the gas content of scrap is that scrap is generally added in greatest bulk at the commencement of the charge, and much of the gas is lost in the act of melting down.

As would be expected, scrap produced in the authors' own works has a lower gas content than that which they have received from elsewhere and which has had, in consequence, an extended period of atmospheric exposure. The form of the gas-containing constituent of steel scrap has received the authors' attention, and the investigations lead them to believe that ingot and forged materials are protected by a high-temperature oxide and keep well, whilst the corrosion product on steel scrap generally is largely hydrated oxide.

Ferro-Silicon and Calcium Silicide (Table XLII.).

Ferro-silicon is supplied in a wide range of composition from 25% to 85% silicon. The higher-silicon alloys are low in carbon (0.05%) as well as in density, and have a brittleness and appearance

TABLE XLII.—*Gas Contents of Ferro-Silicon and Calcium Silicide.*

Material.	Labora- tory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Ferro-silicon :					
85% Si	B.F.R.L.	0-001	0-0024	27	0-0005
80% Si	B.F.R.L.	0-014	0-0038	42	0-0005
80% Si, another sample	B.F.R.L.	0-004	0-0017	19	0-0005
80% Si, another sample	B.F.R.L.	0-005	0-0011	12	0-0005
78% Si	B.F.R.L.	0-005	0-0007	8	0-001
76% Si	N.P.L.	0-005	0-0005	6	0-004
75% Si	N.P.L.	0-021	0-0008	9	0-005
75% Si, another sample	N.P.L.	0-036	0-0008	9	0-003
75% Si, another sample	N.P.L.	0-028	0-0008	9	0-004
45% Si	B.F.R.L.	0-003	0-0007	8	0-001
45% Si	N.P.L.	0-016	0-0007	8	0-001
45% Si, another sample	N.P.L.	0-013	0-0008	9	0-001
45% Si, another sample	N.P.L.	0-017	0-0008	9	0-001
25% Si, 0-8% C	N.P.L.	0-002	0-0002	2	0-002
Calcium silicide :					
60% Si, 32% Ca, 4% Fe	B.F.R.L.	0-065	0-0034	38	0-031

approaching that of elemental silicon. As supplied commercially, ferro-silicon tends to be very porous, often with rounded cavities having bright interiors, and, as would be expected in consequence, the hydrogen content is variable and often very high.

The high oxygen and hydrogen contents of the calcium silicide

TABLE XLIII.—*Gas Contents of Ferro-Chrome.*

Type of Ferro-Chrome.	Labora- tory.	Oxygen. %.	Hydrogen.		Nitrogen. %
			%.	Ml. per 100 g.	
65% Cr, 0-5% C	B.F.R.L.	0-177	0-0012	13	0-014
72% Cr, 8% O, 1% Si	B.F.R.L.	0-016	0-0016	18	0-004
71% Cr, 0-08% C, 0-5% Si	N.P.L.	0-011	0-0005	6	0-039
70% Cr, 0-15% C, 1% Si	N.P.L.	0-056	0-0006	7	0-020
69% Cr, 5-7% C, 2% Si	N.P.L.	0-021	0-0002	2	0-012
65% Cr, 1-2% C, 5-9% Si	N.P.L.	0-022	0-0004	4	0-038
71% Cr, 0-06% C, 0-6% Si	N.P.L.	0-027	0-0005	6	0-051
70% Cr, 0-04% C, 1% Si	C.R.D.	0-012	0-0002	2	0-033
	C.R.D.	0-014	0-0004	4	0-054
	N.P.L.	0-018	0-0013	14	0-067
70% Cr, 0-06% C	B.F.R.L.	0-046	0-0005	6	0-003
	C.R.D.	0-021	0-0003	4	0-029
69% Cr, 0-13% C, 0-6% Si	C.R.D.	0-044	0-0004	5	0-035
	N.P.L.	0-045	0-0019	21	0-034
70% Cr, 0-14% C, 1% Si	C.R.D.	0-058	0-0002	2	0-016
	N.P.L.	0-056	0-0006	7	0-020
71% Cr, 0-08% C, 0-5% Si	C.R.D.	0-017	0-0005	6	0-056
	C.R.D.	0-019	0-0003	3	0-027
	N.P.L.	0-011	0-0005	6	0-039
68% Cr, 0-1% C, 0-1% Si	C.R.D.	0-171	0-0003	3	0-005
75% Cr, 0-07% C, 0-02% Si	C.R.D.	0-329	0-0002	2	0-036
65% Cr, 0-06% C, 0-06% Si	C.R.D.	0-362	0-0002	2	0-010
73% Cr, 0-03% C, 0-09% Si	C.R.D.	0-180	0-0012	13	0-102
	C.R.D.	0-225	0-0008	9	0-123
70% Cr, high-nitrogen	B.F.R.L.	0-70
70% Cr, high-nitrogen, another sample	B.F.R.L.	0-66

are probably accounted for by the presence of a small amount of hydrated lime.

Ferro-Chrome (Table XLIII.).

In the manufacture of rust-, acid- and heat-resisting steels large amounts of chromium are introduced into the steel-melting bath, and it therefore becomes a matter of interest to know how the gas content of the steel is affected by the chromium addition. The heterogeneous condition of many ferro-chrome samples is illustrated by some of the check figures given in Table XLIII. Chromium is a metal which has a considerable affinity for nitrogen, and use is made of this fact, particularly in America, in the production of high-nitrogen steels, for which greatly improved qualities are claimed. The nitrogen content of commercial high-nitrogen ferro-chrome usually approaches 1% of the chromium content. With a typical value of nitrogen for high-nitrogen ferro-chrome of 0.66% it is difficult to obtain accurate values for the oxygen and hydrogen, since they are relatively so small. The authors thus find it better to determine the nitrogen content of such ferro-chromes by the chemical method, and the figures reported in Table XLIII. were obtained in this manner.

Ferro-Manganese, Spiegel and Silico-Manganese (Table XLIV.).

Great importance is attached to the gas content of these materials, together with that of ferro-silicon, as they are added as finishings to

TABLE XLIV.—*Gas Contents of Ferro-Manganese, Spiegel and Silico-Manganese.*

Type and Condition of Manganese Alloy.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Ferro-manganese :					
78% Mn, 7% C, 1% Si . . .	N.P.L.	0.083	0.0036	40	0.024
After 3 hr. at 600° C. . .	N.P.L.	0.35	0.0016	18	0.023
77% Mn, 6.6% C, 0.7% Si . . .	N.P.L.	0.22	0.0075	84	0.036
After 3 hr. at 600° C. . .	N.P.L.	0.58	0.0061	68	0.041
77% Mn, 6.6% C, 0.7% Si (sand cast)	N.P.L.	0.087	0.012	133	0.039
75% Mn, 6.7% C, 0.3% Si (cupola remelt)	N.P.L.	0.065	0.0053	60	0.040
82% Mn, 0.5% C, 1.6% Si, 0.2% P . . .	N.P.L.	0.029	0.0021	22	0.014
After 3 hr. at 600° C. . .	N.P.L.	0.11	0.0024	27	0.014
83% Mn, 0.4% C, 1.7% Si . . .	N.P.L.	0.052	0.0031	35	0.014
78% Mn, 6.7% C . . .	B.F.R.L.	0.036	0.0034	38	0.022
85% Mn (refined manganese)	B.F.R.L.	0.008	0.0026	29	0.002
80% Mn, 1.8% C, 1.4% Si . . .	B.F.R.L.	0.012	0.0048	53	0.001
Silico-manganese :					
70% Mn, 22% Si . . .	N.P.L.	0.039	0.0065	73	0.039
69% Mn, 0.8% C, 23% Si . . .	B.F.R.L.	0.18	0.0072	80	0.019
Spiegel :					
8.5% Mn, 2% Si . . .	N.P.L.	0.13	0.0053	60	0.025
11% Mn, 5% C . . .	B.F.R.L.	0.16	0.0042	47	0.015

steel at the end of the heat and a short time before the teeming of the ingots and the consequent solidification of the steel. Such gas as is added with finishings has less opportunity of being eliminated.

The effect of manganese upon the determination of oxygen by the vacuum fusion method was investigated by Thanheiser¹ and is well known to all who have used this method. The effect is to lower the apparent oxygen value, by a mechanism involving volatilisation of metallic manganese and the subsequent formation of manganese oxide at cooler parts of the apparatus. It would be expected that any volatile and easily oxidised metal would behave similarly, and aluminium certainly exhibits a similar effect, as stated

TABLE XLV.—*Gas Contents of Other Ferro-Alloys.*

Ferro-Alloy.	Laboratory.	Oxygen. %.	Hydrogen.		Nitrogen. %.
			%.	Ml. per 100 g.	
Ferro-molybdenum :					
72% Mo (coarse lumps) . . .	B.F.R.L.	0.020	0.0004	4	0.006
73% Mo	N.P.L.	0.17	0.0010	11	0.011
68% Mo (coarse lumps) . . .	B.F.R.L.	0.036	0.0003	3	0.003
Ferro-titanium :					
23% Ti, 0.07% C	N.P.L.	0.12	0.0013	15	0.022
40% Ti, 0.06% C (crushed to $\frac{1}{4}$ -in. pieces)	B.F.R.L.	0.13	0.0032	36	0.015
Ferro-tungsten :					
80% W, 0.04% C (crushed to $\frac{1}{4}$ -in. pieces)	B.F.R.L.	0.18	0.0002	2	0.001
81% W, 0.05% C (powder) . . .	N.P.L.	0.89	0.0033	37	0.090
85% W, 0.08% C (coconut size) .	N.P.L.	0.21	0.0005	5	0.019
80% W, 0.04% C (crushed to $\frac{1}{4}$ -in. pieces)	B.F.R.L.	0.077	0.0002	2	0.003
Ferro-vanadium :					
50% V, 0.08% C (coarse lumps) .	B.F.R.L.	0.065	0.0019	21	0.009
58% V, 0.1% C	N.P.L.	0.022	0.0010	11	0.014

above in dealing with this metal. To overcome this difficulty for the satisfactory determination of the oxygen content of ferro-manganese, the sample should be highly diluted in a bath of molten iron. Marshall and Chipman² have recommended that such determinations should be made after a certain amount of metallic tin has been volatilised in the furnace and so allowed to coat the cooler parts.

Speaking generally, manganese alloys are high in hydrogen, and are often in a very oxidised state also. The loss of hydrogen on heat-treating to a temperature of 600–700° C. in air is very slow, and is accompanied by considerable oxidation. Assisting the hydrogen diffusion by grinding the ferro-manganese before heat

¹ *Journal of The Iron and Steel Institute*, 1936, No. II., pp. 359 P–392 P.

² *Transactions of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division*, 1940, vol. 140, pp. 127–131.

treatment results in a far more rapid loss of hydrogen, but the extent of oxidation under these circumstances is substantial.

Other Ferro-Alloys (Table XLV.).

Viewed in relation to the quantities used in alloy steel manufacture, the gas contents of the remaining ferro-alloys listed in Table XLV. are not often important. Frequently these ferro-alloys are supplied in a fine, or even ground, condition, and for this and other reasons incidental to their manufacture they frequently contain large amounts of oxygen. This is particularly so with ferro-titanium and ferro-tungsten, the significance of oxide in the former, however, being of importance only as affecting the amount of titanium metal introduced into the bath, since its oxide is not reduced under steelmaking conditions.

Lime, Limestone, Ore, Spar, &c.

It must be recognised that all of these materials which may be added to the steel-melting bath, often in large amounts, are normally in a more or less damp condition. Moisture determinations show that several per cent. of water can be present; whilst most of this can be easily dried out before use if so desired, lime contains combined water which can be eliminated only by roasting before use. This is one of the reasons why, on occasions, limestone can be preferable to lime.

There is really little point in determining the oxygen content of these materials by vacuum fusion, owing to the known large amounts present. Most of this oxygen is, moreover, held in stable form in combination with calcium, magnesium or aluminium, and is not eliminated by the steel-melting reactions. The oxygen content of ores is usually determined by the more conventional chemical methods.

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(e) *THE BEHAVIOUR OF THE OXIDE CONSTITUENTS OF SLAGS IN METHODS OF ANALYSIS FOR OXYGEN IN STEEL.*¹

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SYNOPSIS.

Experiments with five well-known methods for the determination of oxygen in iron and steel are described and studied in relation to their applicability to the determination of oxygen in slag particles in ferrous materials. The method of examination is the "synthetic addition" principle, in which the process is conducted in the presence of a definite weight of slag and the normal weight of N.P.L. oxygen-free iron (Mark 2). An account is given of experimental difficulties associated with this method of examination.

The investigation confirms views previously expressed, in that the acid slag gives good results, whilst the basic slag yields incomplete recovery of its oxygen content on account of either the chemical instability or the refractory character of lime and magnesia compounds.

Much work has been done on the inclusions occurring in steel, and, while under certain circumstances these may include particles of entrapped slag, little work has been done on the response of actual furnace-slag inclusions to the various methods of oxygen determination. With this object in view, experiments have been conducted in a co-operative manner by Members of the Sub-Committee, using two typical slag samples, one acid and the other basic. The methods examined and the co-operating laboratories are as follows :

- (a) *The vacuum fusion method*, by—
 - (1) The United Steel Companies, Ltd., Central Research Department.
 - (2) The Brown-Firth Research Laboratories.
- (b) *The residue methods* :
 - (1) *The alcoholic iodine method*, by—
 - (i) The United Steel Companies, Ltd., Central Research Department.
 - (ii) Messrs. John Lysaght, Ltd.
 - (2) *The chlorine method*, by—
 - Messrs. Stewarts and Lloyds, Ltd.
 - (3) *The aqueous iodine method*, by—
 - The British Cast Iron Research Association.
- (c) *The aluminium reduction method*, by—
 - (1) Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd.
 - (2) The United Steel Companies, Ltd., Central Research Department.

¹ A communication from the Central Research Department, The United Steel Companies, Ltd. (Stocksbridge, Sheffield), received January 22, 1943.

Materials Examined.

Two typical acid and basic open-hearth slags were selected and ground to pass a 100-mesh sieve. After drying at 110° C., the analysis was determined by the British Cast Iron Research Association, with the results given in Table XLVI.

TABLE XLVI.—*Composition and Calculated Oxygen Content of the Slag Samples.*

	Acid Slag.		Basic Slag.	
	Oxide. %.	Oxygen. %.	Oxide. %.	Oxygen. %.
SiO ₂	57.38	30.570	15.62	8.322
FeO	20.48	4.561	7.71	1.718
Fe ₂ O ₃	5.07	1.524
Al ₂ O ₃	1.55	0.730	3.85	1.814
TiO ₂	0.80	0.320	0.54	0.216
MnO	11.56	2.608	3.92	0.884
CaO	7.25	2.068	53.71	15.330
MgO	0.45	0.179	3.64	1.444
P ₂ O ₅	0.07	0.039	5.16	2.910
V ₂ O ₅	Nil	...	0.30	0.132
Total	99.54	41.08	99.32	34.30

In order to reproduce as completely as possible the exact conditions of the particular method of determining oxygen in steel, the presence of a certain weight of iron in these experiments was necessary. It was decided to use a very pure material and the thanks of the Oxygen Sub-Committee are due to the National Physical Laboratory for kindly making available for this purpose a

TABLE XLVII.—*Chemical Analysis and Oxygen Content of Oxygen-Free Iron Bar, N.P.L. Iron, Mark 2.*

<i>Typical Chemical Analysis of Ingot.</i>					
Carbon	. 0.005%	Sulphur	. 0.001%	Copper	. 0.0093%
Manganese	. Nil	Phosphorus	. 0.015%	Magnesium	. 0.0015%
Silicon	. 0.0018%	Nickel	. 0.0019%	Aluminium	. 0.0003%
Oxygen content of $\frac{7}{16}$ -in. dia. bar 0.0005%					

plentiful supply of low-oxygen-content iron in the form of $\frac{7}{16}$ -in. dia. bar. Analysis of this iron and oxygen determinations by the vacuum fusion method at the National Physical Laboratory are shown in Table XLVII., whilst further details, such as preparation, are discussed in the paper by Sloman and Cook, Section III.(a), of this Report.

Oxygen Methods Examined and Details of Procedure.

The general principle of the examination was that of conducting synthetic oxygen determinations on samples consisting of a definite weight of slag sample and the prescribed amount of N.P.L. iron (Mark 2), although in certain cases additional experiments were effected. Brief details of the experimental technique, the results obtained and comments thereon are given in the following.

(a) The Vacuum Fusion Method.

(1) *Experiments at the Central Research Department, The United Steel Companies, Ltd.*—The procedure of adding the slag sample to the vacuum fusion furnace was the "capsule" method. The normal vacuum fusion specimen, *i.e.*, a cylinder, 22 mm. long \times 10 mm. in dia., was drilled longitudinally, giving a cavity of about 5 mm. dia., closed by a tightly fitting plug. These capsules were then charged with a definite weight of dried slag sample. The required weight of slag could be charged into one such capsule; hence, in order to

TABLE XLVIII.—*Determination of Oxygen in the Acid and Basic Slags by the Vacuum Fusion Method.*

(Experiments at the Central Research Department, The United Steel Companies, Ltd.)

Weight of N.P.L. iron (Mark 2) : 25 g. Method : Seventh Ingot Report, p. 65. Temperature of reduction : 1620° C. Blank due to pure iron : 0.0005% of oxygen.				
	Acid Slag.		Basic Slag.	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.
Weight of slag used. G.	0.0400	0.0208	0.0404	0.0200
Weight of oxygen (theoretical). G.	0.01643	0.00854	0.01386	0.00686
Oxygen content of slag (calculated). %	41.08		34.30	
Oxygen content of steel (calculated). %	0.065 ₅	0.034	0.055 ₅	0.027 ₅
Weight of oxygen reduced. G.	0.01516	0.00838	0.00614	0.00306
Oxygen content of slag (determined). %	37.9	40.3	15.2	15.3
Oxygen content of steel (determined). %	0.060 ₅	0.033 ₅	0.024 ₅	0.012
Available oxygen reduced. %	92	98	44	45

reproduce the precise conditions of the usual determination with this apparatus (in respect to weight of steel melted, &c.), in each determination two sample pieces, one solid specimen and one hollow

capsule containing the slag sample, were used. Blank tests with a similar pair of specimens, but without the slag addition, were conducted and the results shown in Table XLVIII. have been corrected for this blank. The remaining experimental details are as described in the Seventh Ingot Report (p. 65).

The following comments are made on the results given in Table XLVIII. :

(a) The acid slag undergoes almost complete reduction under the conditions of the vacuum fusion process. Assuming that all the constituents of the acid slag are present initially as oxides, an average of two tests gives approximately 95% reduction of the available oxygen present. The apparent slight failure to achieve complete recovery may be due either to small experimental errors or to non-reduction of the more refractory oxides, *i.e.*, lime and magnesia.

(b) The basic slag shows a reduction of approximately 45% of the available oxygen. The chemical analysis of this slag gives 34.3% of oxygen, of which 16.77% is associated with calcium and magnesium, leaving a balance of 17.53% of oxygen for the remaining oxides. After making due allowance for the assumptions involved, the fact that 15.3% of oxygen undergoes reduction suggests strongly that calcium and magnesium oxides are not reduced by carbon under the conditions of the vacuum fusion process.

In view of this second conclusion, additional vacuum fusion tests were carried out, using a higher reduction temperature, with the results given in Table XLIX. These show that at the higher temperature a greater proportion of the basic slag is reduced by carbon. The course of the reduction in these tests had interesting features, in that the temperature of reaction was first of all held at 1600–1650° C. until the rate of evolution of gas had decreased and the base pressure was almost equal to that before reduction of the sample. The temperature was then increased and in the case of the acid slag only a very slight increase in gas evolution was evident, decreasing rapidly to the base pressure. With the basic slag, reduction at 1650° C. evolved gas at a rate which gradually decreased to a small value; on increasing the temperature to 1750–1800° C., further rapid evolution of gas occurred and decreased quickly to a very small base pressure. However, although the higher temperature of 1800° C. gives an additional reduction equal to about 30% of the oxygen content of the basic slag, complete recovery of oxygen is not obtained.

(2) *Experiments at the Brown-Firth Research Laboratories.*—Vacuum fusion experiments were also carried out at the Brown-Firth Research Laboratories, with the results shown in Table L. The normal vacuum fusion technique in operation at these Labora-

TABLE XLIX.—*Determination of Oxygen in the Acid and Basic Slags by the Vacuum Fusion Method at High Temperature.*

(Experiments at the Central Research Department, The United Steel Companies, Ltd.)

Weight of N.P.L. iron (Mark 2): 25 g. Temperature of reduction: 1800° C. Blank due to pure iron: 0.0005% of oxygen.				
	Acid Slag.		Basic Slag:	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.
Weight of slag. G.	0.0579	0.0174	0.0376	0.0209
Weight of oxygen (theoretical). G.	0.02379	0.00715	0.01290	0.00717
Oxygen content of slag (calculated). %	41.08		34.30	
Oxygen content of steel (calculated). %	0.095	0.028 ₅	0.051 ₅	0.028 ₅
Weight of oxygen reduced. G.	0.02247	0.00690	0.01007	0.00478
Oxygen content of slag (determined). %	38.80	39.64	26.77	22.83
Oxygen content of steel (determined). %	0.090	0.027 ₅	0.040 ₅	0.019
Available oxygen reduced. %	94.5	96.5	78.0	66.5

tories (Eighth Ingot Report, p. 97) was applied, using a reduction temperature of 1600–1650° C.

The results in Table L. confirm those of Table XLVIII., and al-

TABLE L.—*Determination of Oxygen in the Acid and Basic Slags by the Vacuum Fusion Method.*

(Experiments at the Brown-Firth Research Laboratories.)

	Acid Slag.			Basic Slag.			
	Exp. 1.	Exp. 2.	Exp. 3.	Exp. 1.	Exp. 2.	Exp. 3.	Exp. 4.
Weight of slag. G.	0.0156	0.0194	0.0191	0.0316	0.0294	0.0199	0.0199
Weight of oxygen (theoretical). G.	0.00640	0.00796	0.00781	0.0108	0.0101	0.00681	0.00681
Weight of iron. G.	55	25	40	65	60	45	60
Oxygen content of slag (calculated). %	41.08			34.30			
Oxygen content of steel (calculated). %	0.011 ₅	0.031 ₅	0.019 ₅	0.016 ₅	0.016 ₅	0.015 ₁	0.011 ₅
Weight of oxygen reduced. G.	0.00534	0.00656	0.00615	0.00353	0.00260	0.00173	0.00207
Oxygen content of slag (determined). %	34.6	33.9	32.3	11.2	8.85	8.65	10.4
Oxygen content of steel (determined). %	0.009 ₇	0.026 ₅	0.015 ₄	0.005 ₄	0.004 ₅	0.003 ₅	0.003 ₅
Available oxygen reduced. %	84	82	79	33	26	25	30

though the recovery of oxygen from both slags is not quite so high as in the previously reported tests, the order of recovery is quite similar. Variations of this nature between different operators are to be expected, owing to the experimental difficulties associated with this type of work. Although the slag samples were agate-ground, it is extremely probable that the particle size is greater than that of the naturally-formed inclusion, and, moreover, with tests of this type, involving an addition of slag to an iron specimen, there is a probability that "clotting" of the particles occurs and so retards reduction.

(b) *The Residue Methods.*

Experiments were also conducted to determine the solubility of the acid and basic slags in the different types of solvent used for the alcoholic and aqueous iodine methods. The reaction of the slag samples to the chlorine method was also investigated.

TABLE LI.—*Alcoholic Iodine Method Determinations of Acid and Basic Slags.*

(Experiments at the Central Research Department. The United Steel Companies, Ltd.)

Weight of N.P.L. iron (Mark 2) : 10 g. Weight of slag : 0.1 g. Method : Third Report of the Oxygen Sub-Committee, p. 352P. Boiling time : 8 hr.				
	Acid Slag.		Basic Slag.	
	Residue from Alcoholic Iodine Determination.	Untreated Slag.	Residue from Alcoholic Iodine Determination.	Untreated Slag.
Total ignited residue. G. .	0.1003	0.1011	0.0910	0.0998
Analysis of residue (percentage of slag addition) :				
SiO ₂ . %	54.7	56.3	13.3	15.1
FeO. %	17.6	18.2	12.3	12.1
Al ₂ O ₃ . %	2.0	2.4	3.6	3.2
MnO. %	11.7	11.6	3.4	3.2
CaO. %	7.6	7.4	46.4	54.9
MgO. %	0.7	0.6	3.6	3.8
TiO ₂ }	Not determined.			
V ₂ O ₅ }				
P ₂ O ₅ }				

(1) *The Alcoholic Iodine Method.*—(i) *At the Central Research Department, The United Steel Companies, Ltd.,* the experimental technique used was the "simplified boiling method,"¹ the samples

¹ Stevenson and Speight, Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. 1., p. 352 P.

consisting of 10 g. of N.P.L. iron (Mark 2) in the form of thin discs of $\frac{7}{16}$ -in. bar together with 0.1 g. of slag. After solution, the residue was filtered and analysed. To ensure strict comparison of the analytical results for this residue with the original slag, an equal weight of slag was ignited and parallel analyses were conducted on the two residues, *i.e.*, one residue after alcoholic iodine treatment and the other without that treatment. Similar blank determinations, using the N.P.L. iron (Mark 2) only, were made and the results shown in Table LI. have been corrected for this blank.

The results given in Table LI. lead to the following deductions :

(a) Inclusions of an acid-slag character are almost completely insoluble in the alcoholic iodine solvent. The slight loss in the total ignited residue is of the order of 1% and the analysis of the recovered residue is almost identical with that of the untreated slag. This small loss is possibly an experimental loss or is due to a slight decomposition of iron silicates.

(b) The solution loss with the basic slag is somewhat greater, being of the order of 10%; it occurs mainly in the calcium oxide constituent and to a lesser extent in the silica fraction. It was suggested that the quantity of calcium oxide dissolved by the alcoholic iodine solvent may represent the "free lime" present in the slag, and a few further experiments were carried out to investigate this possibility.

One-gramme portions of slag alone were treated with boiling alcoholic iodine for 3 hr. and filtered, and the calcium content of the filtrate was determined. Results of 12.3% and 11.65% of calcium oxide were obtained, these being slightly higher than the calcium oxide dissolved in the previous tests. Determinations of the free-lime content of the basic slag by a method based on the solubility of calcium oxide in ethylene glycol¹ gave results of 2.60% and 2.48% of calcium oxide. It must therefore be concluded that alcoholic iodine is not a suitable solvent for the determination of free lime in basic slag, since other calcium compounds are attacked to some extent. Moreover, since the amount of lime dissolved by these later tests is greater than that in the previous tests, it would appear that the extent of the decomposition with basic slag might, occasionally, be somewhat higher than that indicated by the original tests. This conclusion is borne out by the repeat determinations on the basic slag shown in Table LII.

(ii) *At Messrs. John Lysaght, Ltd.*, similar alcoholic iodine determinations were carried out with the basic slag only; the experimental technique was that described by Stevenson and Speight in the Third Report of the Oxygen Sub-Committee and the results obtained are given in Table LIII.

¹ Schläpfer and Berger, *Eidgenössische Materialprüfungsanstalt an der E.T.H. in Zürich*, 1933, Report No. 67, p. 16.

TABLE LII.—*Alcoholic Iodine Method Determinations on Basic Slag.*

(Experiments at the Central Research Department, The United Steel Companies, Ltd.)

Weight of N.P.L. Iron (Mark 2) : 10 g. Method : Third Report of the Oxygen Sub-Committee, p. 352P. Boiling time : 10 hr.			
	Exp. 1.	Exp. 2.	Untreated Slag.
Weight of slag. G.	0.2	0.1	0.1
Total ignited residue. G.	0.1795	0.0885	0.0998
Analysis of residue (percentage of slag addition) :			
SiO ₂ . %	12.4	11.8	15.1
FeO. %	13.8	13.2	12.1
Al ₂ O ₃ . %	2.7	2.9	3.2
MnO. %	3.2	3.1	3.2
CaO. %	40.8	42.0	54.9
MgO. %	4.4	4.6	3.8
TiO ₂ } V ₂ O ₅ } P ₂ O ₅ }	Not determined.		

The results of the basic slag experiments, given in Table LIII., show that decomposition by the alcoholic iodine solvent, in both the presence and the absence of iron, has occurred to a greater extent than in the authors' experiments. It is thus obvious that basic slag is unstable under the conditions of the alcoholic iodine deter-

TABLE LIII.—*Alcoholic Iodine Method Determinations on Basic Slag.*

(Experiments at Messrs. John Lysaght, Ltd.)

	Experiments in Absence of Iron.			Experiments in Presence of N.P.L. Iron (Mark 2).		
	Exp. 1.	Exp. 2.	Untreated Slag.	Exp. 3.	Exp. 4.	Untreated Slag.
Weight of slag. G.	0.2000	0.2000	0.2000	0.1000	0.2000	0.2000
Weight of iron. G.	Nil	Nil	...	10	10	...
Boiling time. Hr.	6	6	...	7	10	...
Method	Third Report of the Oxygen Sub-Committee, 1941, p. 352P.					
Total ignited residue. G.	0.0818	0.0554	0.2000	0.0420	0.0763	0.2000
Analysis of residue (percentage of slag addition) :						
SiO ₂ . %	4.15	1.45	14.8	2.0	2.0	14.8
FeO. %	11.75	10.15	12.6	13.0	13.85	13.05
Al ₂ O ₃ . %	1.65	1.10	3.8	2.6	2.8	3.6
MnO. %	2.45	2.7	3.6	2.4	1.35	3.85
CaO. %	15.0	7.8	55.5	13.0	9.9	54.35
MgO. %	2.5	2.15	3.8	3.3	3.0	3.8
P ₂ O ₅ . %	2.8	1.8	5.4	4.7	5.1	5.5

mination and the degree of instability is variable and affected by small differences which exist in the co-operating laboratories.

It must be concluded that, whilst the alcoholic iodine method is satisfactory for the recovery of inclusions of an acid character, inclusions of a basic type undergo decomposition.

(2) *The Chlorine Method.*—At Messrs. *Stewarts and Lloyds, Ltd.*, tests were carried out by the normal method¹ of chlorination at 350° C. and extraction of the residue in both the presence and the

TABLE LIV.—*Chlorine Extraction Method Determinations on Acid and Basic Slags.*

(Experiments at Messrs. *Stewarts and Lloyds, Ltd.*)

Form of sample: 2-mm. discs of $\frac{3}{8}$ -in. bar. Chlorine method: Third Report of the Oxygen Sub-Committee, p. 352P. Chlorination temperature: 350° C.							
	Acid Slag.			Basic Slag.			
	Original Analysis.	Exp. 1.	Exp. 2.	Original Analysis.	Exp. 1.	Exp. 2.	
Weight of slag. G.	0.0194	0.0103	...	0.0124	0.0211	
Weight of iron. G.	Nil	10	...	Nil	10	
Total ignited residue. G.	0.0200	0.0107	...	0.0074	0.0139	
Analysis of residue (percentage of slag addition):							
SiO ₂ . %	57.38	54.91	52.43	15.62	12.07	11.11	
FeO. %	20.48	19.30	19.14	12.27	14.18	14.94	
Al ₂ O ₃ . %	1.55	1.72	1.92	3.85	2.11	2.43	
MnO. %	11.56	11.65	11.19	3.92	2.64	3.00	
TiO ₂ . %	0.80	0.72	0.78	0.54	0.32	0.33	
V ₂ O ₅ . %	Nil	Not determined.		0.30	Not determined.		
Cr ₂ O ₃ . %	0.31	0.25	...	0.45	0.38	
P ₂ O ₅ . %	0.07	0.11	0.15	5.16	4.38	4.13	
CaO. %	7.25	8.71	6.93	53.71	20.12*	22.57*	
MgO. %	0.45	1.03	0.97	3.64	1.61*	1.89*	
* The filtrates obtained after extraction of the chlorinated residue were examined for calcium and magnesium, and the following amounts were recovered:							
CaO. %					34.17	34.05	
MgO. %					0.50	0.44	

absence of N.P.L. iron (Mark 2), with the results given in Table LIV., on which the following comments are made:

(a) The acid slag shows very little modification of either quantity or composition as a consequence of the chlorine extraction treatment. The small increase in weight of the ignited residue is probably due to increase in the oxidation of iron oxide during ignition. Calculation of the oxygen content of the residue gives values of 40.36% and 38.46%, which, compared with the original oxygen content of 41.08%, indicates

¹ Colbeck, Craven and Murray, Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 332 P.

a recovery of 98% and 94%, respectively. Hence the behaviour of acid slags in the chlorine method is precisely similar to that in both the alcoholic iodine and the vacuum fusion methods.

(b) Following the normal chlorine method, the basic slag, on the other hand, shows a considerable loss in the ignited-residue result, this loss being chiefly reflected in the low recovery of lime and magnesia. However, the balance of these oxides is recovered almost completely from the filtrates after the initial extraction of the chlorinated residue with water. Tests have also been carried out to investigate the possibility of this amount of lime being present as "free lime," but determinations of this constituent by the method of Lerch and Bogue¹

TABLE LV.—*Aqueous Iodine Extractions on Acid and Basic Slags.*
(Experiments at the British Cast Iron Research Association.)

Weight of N.P.L. iron (Mark 2): 5.0 g. (turnings). Weight of slag used: 0.1 g. Method: Third Report of the Oxygen Sub-Committee, p. 358P.						
	Acid Slag.			Basic Slag.		
	Original Analysis.	Exp. 1.	Exp. 2.	Original Analysis.	Exp. 1.	Exp. 2.
Total ignited residue. G.	...	0.04661	0.04546	...	0.004989	0.00534
Analysis of residue (percentage of ignited residue):						
SiO ₂ . %	57.38	58.83	57.79	15.62	The above residues consisted essentially of alumina.	
FeO. %	20.48	17.77	19.01	7.71		
Fe ₂ O ₃ . %	5.07		
MnO. %	11.56	8.51	9.35	3.92		
Al ₂ O ₃ . %	1.56	1.14	Not determined.	3.85		
TiO ₂ . %	0.80	0.54		
CaO. %	7.25	8.19	8.09	53.71		
MgO. %	0.45	Not determined.	{	3.64		
P ₂ O ₅ . %	0.07			5.16		
V ₂ O ₅ . %	Nil			0.30		

showed only very small quantities of free lime. It must therefore be concluded that the calcium compounds of basic slag are attacked by chlorine to yield a chloride non-volatile at 350° C. but which is dissolved from the chlorinated residue by the subsequent washing treatment. Inclusions of a basic-slag character would not, therefore, be determined completely by the normal procedure for the chlorine method.

(3) *The Aqueous Iodine Method.*—At the British Cast Iron Research Association the response of these acid and basic slags to the conditions of the aqueous iodine method was investigated, with the results shown in Table LV. The tests were carried out in the

¹ Lerch and Bogue, *Industrial and Engineering Chemistry*, 1926, vol. 18, July, p. 739.

presence of N.P.L. iron (Mark 2) and the results have been corrected for the blank obtained from similar determinations using the low-oxygen iron only.

The following comments are made on the results given in Table LV.:

(a) Under the conditions of the aqueous iodine extraction method for non-metallic inclusions, both the acid and basic slags are attacked.

(b) Whilst approximately 50% of the acid slag is dissolved, the dissolution is not entirely selective, since the composition of the residue approximates closely to that of the original slag. However, there are indications that the attack was slightly more severe on the iron and manganese oxides than on the silica and calcium-oxide constituents.

(c) With the basic slag, the conditions of the aqueous iodine solution or of the subsequent treatments are very severe, in that only 5% approximately of the original addition is recovered, consisting essentially of alumina.

(d) Thus, in the aqueous iodine procedure, non-metallic inclusions of an acid-slag type would be partially extracted and the analysis of this extracted residue would correspond to some extent to that of the original inclusions, whereas inclusions of basic slag would be almost completely soluble. The exact stage at which this dissolution takes place is not clear, since it is possible that much of the attack occurs during the subsequent treatments. It is interesting to compare this result with that given by the chlorine method, since both methods have similarities in the aqueous treatment given to the residue obtained by the halogen attack.

(c) *The Aluminium Reduction Method for Total Oxygen.*

(1) *Experiments at Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd.*—The applicability of the aluminium reduction method¹ to the determination of the total oxygen content of acid and basic slags was studied, with the results given in Table LVI. These show that:

(a) Almost complete conversion of the constituent oxides of the acid slag to alumina is obtained by the aluminium reduction method, and consequently inclusions of this type can be determined with confidence by this method.

(b) On the other hand, approximately 50% of the oxygen content of the basic slag is converted to alumina; hence those inclusions in steel having a constitution similar to the basic slag are not completely measurable by the aluminium reduction

¹ Gray and Sanders, Eighth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1939, *Special Report No. 25*, p. 103.

technique. It must again be pointed out that, since approximately 50% of the oxygen content of the basic slag occurs as calcium and magnesium oxides, there is a definite suggestion that these oxides are not reduced by aluminium.

(2) *Experiments at The United Steel Companies, Ltd.*—The following account of the investigation into the response of these acid and basic slag samples to the aluminium reduction method illustrates very vividly the inherent difficulties associated with this principle of checking the accuracy of methods for the oxygen content of iron and

TABLE LVI.—*The Determination of Total Oxygen on Acid and Basic Slags by the Aluminium Reduction Method.*

(Experiments at Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd.)

Weight of N.P.L. iron (Mark 2) : 10 g. Weight of pure aluminium : 14 g. Form of sample : Discs $\frac{1}{8}$ in. thick. Hydrogen technique : Eighth Ingot Report, p. 103. Blank (10 g. N.P.L. iron (Mark 2) and 14 g. aluminium) : 0.0009 g. of alumina.				
	Oxygen Content of Sample (Theoretical). %.	Weight of Alumina after Correction for Blank. G.	Oxygen Content of Sample (Determined). %.	Recovery of Slag Addition. %.
Acid slag addition :				
(a) 0.0012 g. . .	0.005	0.0010	0.0047	94
(b) 0.0024 g. . .	0.010	0.0021	0.0098	98
(c) 0.0121 g. . .	0.050	0.0103	0.0484	97
(d) 0.0243 g. . .	0.100	0.0210	0.0987	99
(e) 0.0365 g. . .	0.150	0.0310	0.1457	97
Basic slag addition :				
(a) 0.0015 g. . .	0.005	0.0006	0.0028	56
(b) 0.0030 g. . .	0.010	0.0012	0.0056	56
(c) 0.0146 g. . .	0.050	0.0050	0.0235	47
(d) 0.0292 g. . .	0.100	0.0111	0.0522	52
(e) 0.0437 g. . .	0.150	0.0155	0.0728	48

steel, and is placed on record for the benefit of other workers who may be faced with this particular problem. The investigation involved a considerable amount of work, during the course of which doubts were raised regarding the validity of the method, but these were eliminated when a satisfactory technique for the admixture of the slag and metal samples had been developed. Only a brief account of the main steps need be given here, but it must be emphasised again that this considerable amount of work was occasioned solely to overcome the disadvantages revealed by the principle of the synthetic addition method of examination.

Initial experiments were carried out using the normal low-

pressure technique ¹ and samples consisting of the usual two strips of aluminium sheet, between which were placed four thin discs of N.P.L. low-oxygen iron (Mark 2). Shallow depressions were machined in the iron discs and charged with sufficient ground slag to yield 0.05% of oxygen in the total alloy melt. These tests, which were repeated, gave almost negligible weights of alumina residue after acid extraction of the melt. That the fine slag particles had been lost owing to the out-rush of air during evacuation was the immediate explanation, although no evidence to support this theory had been detected. However, tests carried out to investigate this possibility made it certain that the slag could not have been lost in this manner.

It was then believed that, for some reason unknown, the low-pressure technique had failed in its application to these slag samples and that the presence of hydrogen was necessary to ensure quick reduction of the slag particles, which, considered in the light of

TABLE LVII.—*Comparison of Two Aluminium Reduction Procedures on Known Steels.*

(Experiments at the Central Research Department, The United Steel Companies, Ltd.)

Method.	SG1101. Oxygen Content, 0.175%.	SG2618. Oxygen Content, 0.054%.	Appearance of Melt.
Oxygen determined—			
(1) By low-pressure technique	0.155%	0.055%	Good.
(2) In hydrogen atmosphere at 25 cm. pressure.	0.164% 0.157%	0.046% 0.054%	Dull appearance; incomplete alloying.

non-metallic inclusions, represent massive particles. Consequently, modifications were made to the apparatus, whereby the heating was effected in a hydrogen atmosphere at about 25 cm. pressure. After overcoming serious blank troubles, which resulted in residues heavily contaminated with aluminium sulphide and carbide, the recoveries of alumina were slightly better but in no way satisfactory, since a reduction of at least 95% was expected from the acid slag.

Extended trials of both techniques were made on two steels of high oxygen content, the oxygen existing as iron oxide in one sample and manganese silicate in the other.

The results recorded in Table LVII. confirm once again the accuracy of both procedures and show that the modified hydrogen-atmosphere method presents no advantages over the low-pressure technique. It was obvious that the failure to achieve reduction

¹ Stevenson and Speight, Third Report of the Oxygen Sub-Committee, p. 326 P.

of the slags was due, in some manner, to sampling difficulties. Attention was now directed to a close examination of the original low-pressure method.

A further test on the acid slag was now carefully made. After removing the graphite boat from the furnace, small fluffy black residues were seen on the surface of the alloy and in the corners of the boat, quite detached from the melt. The black residues were collected and analysed, showing the presence of silica, iron and manganous oxides, and alumina; thus they consisted of alumina and unchanged slag. The alloy melt analysed separately gave a quantity of alumina equivalent to 10% of the added oxygen. It was apparent that, in some manner, the slag particles floated clear of the melt and so escaped reduction. Careful trials were again made to ensure that the evacuation of the apparatus with the two-stage oil pump was not responsible for this phenomenon, with the result that, even under the worst conditions and after six repeated evacuations,

TABLE LVIII.—*Analysis of Residues from Aluminium Reduction Method on Acid Slag.*

Slag Addition.		Ignited Residue.		Analysis of Residue.				Alumina Recovery. %.
Slag. G.	Oxygen. G.	(a) Before Hydro- fluoric Acid Treat- ment. G.	(b) After Hydro- fluoric Acid Treat- ment. G.	Fe ₂ O ₃ . G.	MnO. G.	Al ₂ O ₃ .		
						Alumina. G.	Oxygen. G.	
0.0096	0.0039	0.0094	0.0094		Analysis not made.			
0.0112	0.0046	0.0094	0.0089	0.0005	0.0002	0.0083	0.0039	85
0.0212	0.0087	0.0190	0.0129	0.0032	0.0008	0.0091	0.0043	49
0.0322	0.0132	0.0292	0.0211	0.0045	0.0017	0.0146	0.0069	52

the slag powder was still undisturbed in the shallow depressions of the pure-iron slices. The movement of the slag particles to the sides of the melt must therefore occur during the fusion and alloying of the iron with the aluminium.

The problem was now resolved into the development of a method for introducing the slag into the metal sample whereby this outward movement of the slag and the subsequent lack of reduction could be obviated. Accordingly, tests were conducted in which the acid-slag powder was packed into tiny holes drilled in the side of the thin iron slips, the holes being finally closed with a small pure-iron plug. It was considered that fusion and alloying of the iron would occur before any movement of the slag took place. In all cases black incrustations of identical size and shape as the tiny holes originally packed with slag were found either detached from the melt or projecting from the sides like the horns on a mine. On analysis

these residues showed the presence of unchanged slag with alumina as the major constituent.

The results, given in Table LVIII., indicate a variable reduction of the slag and that the method adopted for the slag and sample admixture was unsatisfactory. A further method was then tried. Comparative tests with both acid and basic slags were made; in one pair of tests the slag was added as in the previous experiments and in a second set it was added to the aluminium instead of to the iron. A trough was machined in the bottom strip of aluminium, into which the slag was evenly spread, the slotted cavity being closed by a thin aluminium strip of exact size to fit. Pure-iron discs were placed on top, followed by the top aluminium strip as usual. This sample arrangement was then placed in a smaller graphite boat of appropriate size just to accommodate the particular dimensions of the aluminium strip, and by this means it was hoped that, even if the slag was floated to the edges of the melt, it would not become detached from the molten aluminium alloy.

These tests were very encouraging, since analysis showed the residues to be substantially alumina. However, the incrustation was still apparent on the bottom of the melt after being detached from the boat, and it was suspected that some of the incrustation was absorbed into the graphite boat and hence not accounted for in these determinations, since the results were somewhat low. Accordingly the assembly of the sample was revised in the following manner: Slag was added to an aluminium strip as above, and this strip, instead of being the bottom strip adjacent to the graphite boat, was placed on top of the plain strip, which then became the lower part of the arrangement. Pure-iron discs were placed on top of the slag-charged aluminium strip. The order of the assembly from the bottom upwards was therefore:

- (a) Aluminium strip.
- (b) Aluminium strip charged with slag.
- (c) Low-oxygen iron discs.

This arrangement was found to be entirely satisfactory; the melt was bright and had a thin incrustation running along the sides of the specimen. The residue was entirely alumina and a yield of 99% of oxygen was obtained from the acid slags.

Determinations on both the acid and basic slags were then made with this arrangement of aluminium strip and iron discs, with the results shown in Table LIX. These confirm that inclusions of an acid type are converted completely to alumina in the aluminium reduction method and hence their oxygen content is measurable by this method. The reduction of the constituent oxides of the basic slag is very incomplete, in that approximately 15% only of the available oxygen is reduced by this process. It must be concluded, therefore, that inclusions of a basic type cannot be determined by the aluminium reduction method in its present form.

General Summary and Conclusions.

The work reported in this paper is of prime importance in so far as certain limitations of the current methods adopted for the determination of non-metallic inclusions in ferrous materials are related to the actual composition of these inclusions. Apart from such

TABLE LIX.—*Determination of Total Oxygen in Acid and Basic Slags by the Aluminium Reduction Method.*

(Experiments at the Central Research Department, The United Steel Companies, Ltd.)

Weight of N.P.L. iron (Mark 2): 6 g. Weight of pure aluminium: 14 g. Vacuum technique: Third Report of the Oxygen Sub-Committee, p. 326p. Blank (6 g. iron and 14 g. aluminium): 0.0004 g. of alumina.							
Slag Addition.		Oxygen Content of Sample (Theoretical). %.	Weight of Residue after Blank Correction. G.	Analysis of Residue.		Oxygen Content of Sample (Determined). %.	Recovery of Slag. %.
Slag. G.	Oxygen Content. G.			Alumina. G.	Oxygen Content. G.		
Acid Slag.							
0.0202	0.0083	0.138	0.0193	0.0183	0.0086	0.143	103
0.0226	0.0093	0.155	0.0200	0.0197	0.0092	0.154	100
0.0307	0.0126	0.210	0.0270	0.0265	0.0124	0.207	99
Basic Slag.							
0.0311	0.0106	0.177	0.0029	0.023	13
0.0210	0.0072	0.120	0.0025	0.020	16

compounds as sulphides, carbides, &c., it is generally conceded that non-metallic inclusions of a normal killed steel have two or three possible origins :

(a) Reaction products of the deoxidation with silicon, manganese, aluminium, coalescing with ferrous oxide to yield silicates, spinels, &c.

(b) Reaction between ferrous and manganese oxides and refractories of the ladle and casting pit, yielding similar products to (a) above.

(c) Entrapped slag particles, which may be acid or basic, depending on the method of manufacture.

Inclusions of type (a) or (b) are of an acid or neutral character, and it is reasonably certain that these types constitute the large bulk of inclusions occurring in normal steels. The results of this investigation indicate that such inclusions can be determined with confidence by those methods examined. The vacuum fusion and aluminium reduction methods for total oxygen, and the alcoholic iodine and chlorine extractions for non-metallic inclusions yield complete separations, whilst only the aqueous iodine method shows

a loss of the acid-slag type of inclusion. The reason for the apparent loss of acid-slag inclusions in this method, without material change of composition, is a little obscure, and is almost indicative of a mechanical or experimental loss of the residue.

Whilst type (c) inclusions should not occur under the best steel-making conditions, knowledge of their behaviour in these methods of analysis is essential, and is indicated by the subject matter of this paper. As with more normal inclusions, if the slag entrapped is acid in character, its oxygen content is measured by the usual methods. However, when the slag is basic, its oxygen content is not completely measurable. Results by the different co-operating laboratories on this slag have been very inconclusive regarding a quantitative statement of the extent of the reaction in each method. This is undoubtedly due to the inevitable but very slight variations in the test conditions at each laboratory and the resultant effect on the chemically unstable basic slag, and, in addition, to the inherent sampling difficulties. For example, reductions of 45% and 10% are recorded with normal vacuum fusion techniques at different laboratories. The amount of slag reduced increases, of course, with increase of reaction temperature to 1800° C., when approximately 75% of the slag oxygen is reduced by carbon. Again, with the alcoholic iodine method, different operators obtained respectively recoveries of 90% and 40% of the slag addition. The chlorine method showed a recovery of the order of 60%, the loss being mainly in the lime and magnesia constituents. In the aqueous iodine method, the basic slag was completely dissolved with the exception of the alumina fraction, and with the aluminium reduction method reductions of 50% and 15% were recorded by different operators. Viewing these variations broadly, it can be stated that inclusions of the basic-slag type do not yield their entire oxygen content by any of our present methods, the main source of the deviation from complete reduction being that oxygen associated with calcium and magnesium.

This investigation has been of definite assistance in providing practical confirmation of the view held by the Sub-Committee from theoretical considerations, namely, that non-metallic inclusions of the normal type can be determined by the present well-known methods. If entrapped slag particles are present, complete estimation depends entirely upon their nature and particularly on the presence of lime and magnesia slag compounds.

(f) 4% SILICON TRANSFORMER IRON.¹

(Figs. 16 to 18 — Plate XX.)

The examination of 4% silicon transformer iron by the aluminium reduction method for the determination of oxygen was carried out independently but simultaneously at Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd., and Messrs. John Lysaght, Ltd., and calls attention to the production during the alloying with aluminium of a dark substance subsequently identified by analysis and X-ray examination as elemental crystalline silicon. The analytical procedure adopted in the two laboratories varied somewhat, and is described in the following contributions.

(f1) *Behaviour of 4% Silicon Transformer Iron in the Aluminium Reduction Method in a Hydrogen Atmosphere.*

By N. GRAY, M.MET., AND M. C. SANDERS (MESSRS. GUEST KEEN BALDWIN'S IRON AND STEEL CO., LTD., PORT TALBOT).

Modifications in the analytical procedure are described which are designed to eliminate the tendency for precipitation of silicic acid from the hydrochloric acid solution of the alloy. A preliminary study has been made of the formation of elemental crystalline silicon in varying circumstances.

Five grammes of the material were heated with 7 g. of aluminium in the prescribed manner up to the production of the iron-aluminium alloy. The alloy thus produced was then dissolved in 300 ml. of dilute hydrochloric acid (1 : 1) in which 5 g. of citric and tartaric acids were dissolved. The addition of concentrated nitric acid was found to induce the precipitation of silicic acid, which retarded filtration, and the oxidation was therefore omitted, the hydrochloric acid solution being filtered and the residue washed with hot dilute (5%) hydrochloric acid and hot water prior to ignition. The ignited residue was treated with hydrofluoric acid, which, after final ignition, yielded a black constituent equivalent in proportion to 0.2% of the material. This was fused with alkali carbonate fusion mixture, and the alumina, resulting from the reduction of the oxides in the metal, was determined in the acid extract of the fusion in the usual manner.

Treatment of the iron alone in this way, without the preliminary treatment with aluminium, failed to produce this black constituent, indicating its formation during the heating with aluminium.

The possibility of its being due to mechanically detached graphite from the boat or to the reduction of silica in the inclusions by such graphite has since been ruled out by its production in a boat made of pure alumina. This experiment was, of course, of no use for the determination of oxygen and was not so intended.

¹ Received December 16, 1942.

Subsequent chemical analysis and an X-ray examination by Dr. A. H. Jay have indicated that the substance is elemental crystalline silicon.

The percentage formed appears to vary with the thickness of the sample of material used and the temperature at which the alloying is carried out. A short series of experiments was made, the results of which are included in Table LX., together with a microscopic examination of the black residue produced at a temperature of 1200° C. Photomicrographs are shown in Figs. 16 to 18. These

TABLE LX.—4% Silicon Transformer Iron. *Production of Black Elemental Silicon.*

Sample.	Thickness of Metal. In.	Temp. of Heating. ° C.	Black Elemental Silicon obtained. %.
10 g. of material, 14.5 g. aluminium, heated 1½ hr. in hydrogen	$\frac{1}{8}$	1000	0.016
	$\frac{1}{4}$	1000	0.200
	$\frac{3}{8}$	1000	0.260
	$\frac{1}{2}$	1100	0.200
	$\frac{3}{4}$	1200	0.950

indicate that the thickness of the specimen and the temperature at which it is heated with aluminium influence the proportion of elemental silicon displaced from the iron.

Microscopic Examination.—Fig. 16 (polarised light) shows the material to be opaque and of a very angular nature; traces of anisotropic impurities are present.

Figs. 17 and 18 (reflected light and high magnification) show the presence of hexagonal plates. There are indications that the view in Fig. 17 is basal and in Fig. 18 vertical.

(f2) *Behaviour of 4% Silicon Transformer Iron in the Aluminium Reduction Method under Reduced Pressure.*

By C. S. GRAHAM AND C. W. SHORT (MESSRS. JOHN LYSAGHT, LTD., SCUNTHORPE).

When the material was treated by the procedure outlined in the Third Report of the Oxygen Sub-Committee,¹ a greyish black substance was always present in varying amounts in the ignited residue.

This material was not attacked by hydrofluoric-sulphuric acid treatment, but was easily fusible with alkali carbonate, yielding in the subsequent analysis a silicon figure equivalent to the amount of extraneous matter present in the ignited residue. Amorphous silicon being soluble in hydrofluoric acid (Mellor), this suggested

¹ *Journal of The Iron and Steel Institute*, 1941, No. I., p. 326 P.

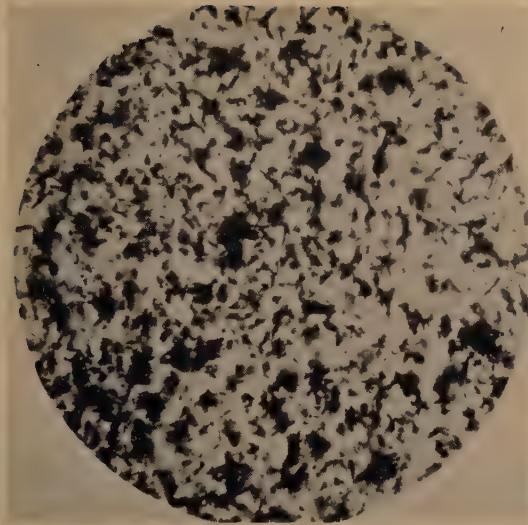


FIG. 16.—The material is opaque and very angular, with traces of anisotropic impurities. Polarised light. $\times 100$.

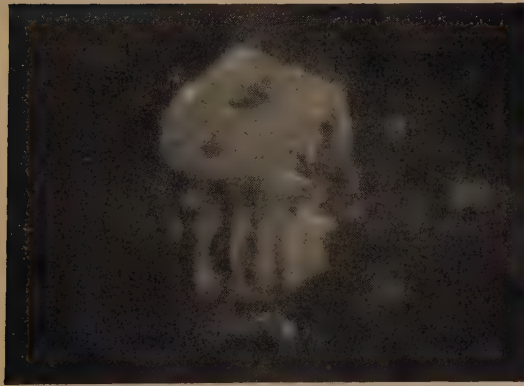


FIG. 17. — Hexagonal plates; view probably basal. Reflected light. $\times 2000$.



FIG. 18. — Hexagonal plates; view probably vertical. Reflected light. $\times 2000$.

FIGS. 16 to 18.—The Black Constituent extracted from 4% Silicon Transformer Iron in the aluminium reduction method (hydrogen atmosphere).

[Fourth Report of the Oxygen Sub-Committee.

[Section III.(f).

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that this substance was crystalline silicon, which, whilst being insoluble in hydrofluoric acid (Mellor), is soluble in a mixture of hydrofluoric and nitric acids (Mellor). The residue was treated with the mixed acids and volatilised. Evaporation and ignition left the alumina free from all extraneous matter.

A suggested explanation may be derived by analogy from the preparation of crystalline silicon from potassium silico-fluoride in molten aluminium. It is definitely not derived from reaction of the silica with aluminium, as the oxygen equivalent to the amount of crystalline silicon present would be far in excess of the oxygen in the steel.

When applying the aluminium reduction method to this material, certain modifications are necessary:

Proceed as on p. 326 P of the Third Report (*loc. cit.*) until the melt is placed in acid; use 600 ml. of hydrochloric acid (1 : 1), and do not oxidise with nitric acid, filter and wash well with 5% hydrochloric acid, followed by two alternate washings with 3% sodium carbonate solution (*hot*) and 5% hydrochloric acid. Finally wash with hot water; ignite the residue at 1000° C. in a tared platinum crucible, add 2 drops of sulphuric acid and 10 c.c. of hydrofluoric acid, and carefully, drop by drop, 5 ml. of concentrated nitric acid. Evaporate to dryness, avoiding any spitting and ignite at 1000° C. Cool and weigh. Fuse the "alumina" with 0.3 g. of sodium-carbonate/potassium-chlorate (2 : 1) mixture, extract the melt with 10% sulphuric acid and estimate the ferric oxide and titanium oxide colorimetrically; subtract the amounts found, if any, from the combined weight after ignition, and the difference is the alumina equivalent to the oxygen in the steel.

(g) OXIDE INCLUSIONS IN BRITISH PIG IRONS.¹

BY J. G. PEARCE, M.Sc., F.INST.P., M.I.MECH.E. (BRITISH CAST IRON RESEARCH ASSOCIATION, ALVECHURCH, BIRMINGHAM).

SYNOPSIS.

The total-oxygen contents of twenty-nine pig irons determined by the aluminium reduction method and of seven of the same group by the vacuum fusion method are recorded. Results for silica, alumina and ferrous oxide by the aqueous iodine method for forty-nine pig irons are given. Neither the total-oxygen nor the individual oxide values show any relationship to the method of manufacture, type, composition or fracture of the pig irons. Some uncertainties of the aqueous iodine method are indicated.

The considerations which led to the study of oxide inclusions in a representative series of British pig irons have already been given,

¹ Received March 1, 1942.

with some preliminary results.¹ Through the interest of the Blast-Furnace Committee of the Iron and Steel Industrial Research Council, over one hundred samples were supplied, about half of which were examined.

On theoretical grounds, the presence of oxides in an iron-carbon alloy such as pig iron is not normally to be expected, but the rarity with which in practice equilibrium conditions are attained precludes our attaching undue importance to deductions based on equilibrium conditions. Furthermore, the presence of inclusions, colloiddally suspended and otherwise, has been so frequently postulated to explain effects requiring, or appearing to require, a nucleating medium that direct attempts, chemical or physical, to determine their presence become desirable.

The results of microscopic examination, referred to in the above-mentioned paper, have been such as to raise the question of the validity of chemical residue methods applied to pig and cast irons. Microscopically, there is no evidence of the presence of oxides or silicates of iron, manganese or aluminium. Nevertheless, foreign inclusions of sand or slag, derived from furnace linings, mould materials or entrapped slags, are readily visible under the microscope, and in irons oxidised in service after being submitted to elevated temperatures the oxide is easily revealed. Inherent inclusions in normal pig irons, therefore, are either absent, or are sub-microscopic, or are dissolved in the metallic or non-metallic phases of the structure. As explained in the earlier paper, sulphides, a very considerable inclusion, are not determined by the residue method. Silicates and aluminates, especially in the small quantities present, may well be dissolved in such sulphides or masked by them.

This microscopic work has resulted in a fresh angle of approach to the question of inclusions in pig iron, and the results of examination by chemical residue methods are now reported, subject to the reservation that this new approach may bring about considerable changes.

The results of the chemical residue examination show that there is no consistent relationship between the oxides present and the chemical composition of pig irons as a whole; neither is there any consistent relationship between oxides in a series of pig irons from the same furnace and their chemical composition or fracture. Similar remarks apply to refined pig irons, and, as far as oxides are concerned, there is no difference between ordinary and refined pig irons. Hence, oxide inclusions determined by the residue method do not offer any basis for differentiating types of pig iron, hematite, foundry, basic, from one another; nor for distinguishing a method of production, as charcoal, cold-blast, hot-blast, refined; nor for differentiating irons of varying compositions and fractures from the same furnace.

¹ Third Report of the Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 366 P.

Table LXI. gives the pig-iron analyses arranged in groups according to phosphorus content, *i.e.*, hematites up to 0.1%, 0.1–0.5%, 0.5–1.0% and above 1.0% of phosphorus, with a group of miscellaneous materials for purposes of comparison. Within the groups,

TABLE LXI.—*Analysis of Pig Irons.*

	No.	Type of Pig Iron.	Analysis of Sample.					
			Si. %.	Mn. %.	S. %.	P. %.	Ti. %.	V. %.
Phosphorus < 0.1%.	69	Spotted white (for malleable).	0.60	0.20	0.100	0.060
	70	Grey (for malleable).	1.10	0.25	0.100	0.050
	68	Forge.	1.66	0.53	0.096	0.022
	65	Semi-special.	1.94	0.65	0.023	0.024
	64	Super-special.	2.33	0.48	0.011	0.018	0.08	Trace
	101	Special hematite.	1.70	1.45	0.020	0.027	0.07	Nil
	38	Hematite.	2.48	1.14	0.010	0.029	0.14	Nil
	102	Hematite.	3.40	1.08	0.017	0.035	0.06	0.06
	16	Hematite.	2.40	0.54	0.020	0.036	0.07	Nil
	107	Hematite.	2.55	1.03	0.003	0.040	0.08	0.03
	109	Refined grey (for malleable).	2.28	0.30	0.073	0.048
	103	Hematite.	3.00	1.57	0.026	0.049
	18	Hematite.	1.70	0.94	0.019	0.053	0.14	0.03
	73	Hematite.	2.33	1.25	0.008	0.067
	35	Charcoal.	2.88	0.13	0.031	0.080	0.02	Nil
Phosphorus 0.1% to 0.5%.	50	Pig iron No. 3, soft.	2.84	1.01	0.027	0.17	0.19	Nil
	75	Cylinder.	0.92	0.88	0.035	0.18	0.01	Nil
	108	Refined (cylinder).	1.29	1.23	0.034	0.18
	23	Refined.	1.99	1.00	0.035	0.26	0.01	0.02
	79	Refined (cylinder).	1.62	0.75	0.053	0.28	0.07	Nil
	24	Refined.	1.90	1.03	0.123	0.29	0.04	0.02
	55	Refined.	1.93	1.09	0.070	0.32	0.04	Nil
	56	Refined.	1.65	0.94	0.056	0.34
	76	Cold-blast.	1.46	0.78	0.095	0.35	0.08	Nil
	88	Refined.	1.55	1.10	0.055	0.37	0.07	0.04
	19	Cold-blast.	1.08	0.62	0.079	0.40	0.04	Nil
	25	Cold-blast.	0.85	0.51	0.088	0.45	0.03	Nil
	26	Cold-blast.	1.28	0.70	0.099	0.54	0.03	Nil
Phosphorus 0.5% to 1.0%.	54	Foundry.	1.25	0.89	0.050	0.61	0.08	0.06
	47	Foundry No. 3.	2.89	0.70	0.029	0.72	0.17	0.18
	86	Foundry No. 3.	2.74	0.82	0.037	0.72	0.17	0.08
	60	Foundry.	4.40	1.02	0.016	0.80
	87	Foundry No. 3.	2.50	1.66	0.040	0.95	0.29	0.11
Phosphorus > 1.0%	30	Foundry No. 3.	2.07	0.71	0.039	0.96
	28	Foundry No. 1.	2.33	0.72	0.022	1.06
	29	Foundry No. 2.	2.34	0.69	0.034	1.05
	31	Foundry No. 4.	2.38	0.30	0.076	0.94	0.16	0.09
	33	Forge No. 4.	2.41	0.35	0.070	1.21
	34	Grey forge.	2.70	0.74	0.076	1.20
	27	Silky.	4.62	0.71	0.029	1.28
	39	Basic.	0.23	2.68	0.021	1.08	0.09	0.07
	111	Foundry No. 3.	2.84	1.05	0.045	1.10
	40	Foundry.	3.19	0.42	0.019	1.15	0.20	0.12
	82	Basic.	0.56	1.45	0.043	1.19	0.05	0.11
	37	Foundry No. 3.	2.39	0.26	0.057	1.26	0.19	0.09
	99	Basic.	0.94	1.46	0.062	1.40	0.06	0.14
	85	Forge.	1.89	0.38	0.058	1.41	0.23	0.17
	21	Basic.	2.86	0.29	0.026	1.42	0.21	0.04
	84	Foundry No. 3.	3.01	0.41	0.023	1.50	0.33	0.10
Miscellaneous Irons.	13	Armco Iron.
	15	Wrought-iron bar.	0.078	0.022	0.010
	14	Swedish iron.	0.20	0.12	0.008	0.036	Nil	Nil
	53	Imatra, Swedish.	0.14	0.21	0.030	0.045	Nil	Nil

the order is of increasing phosphorus content, except that in groups of irons from the same furnace of the same nominal phosphorus content, the order is that of silicon content. Table LXII. gives the total-oxygen figure by aluminium reduction and vacuum fusion for

TABLE LXII.—*Total Oxygen in Pig Irons.*

No.	Oxygen by—		No.	Oxygen by—		No.	Oxygen by—		No.	Oxygen by—	
	Alumin-ium Red-uction.	Vacuum Fusion.		Alumin-ium Red-uction.	Vacuum Fusion.		Alumin-ium Red-uction.	Vacuum Fusion.		Alumin-ium Red-uction.	Vacuum Fusion.
101	0-0043	...	35	0-011	...	19	0-011	0-011	40	0-010	...
38	0-013	...	75	0-014	...	25	0-0084	...	37	0-013	...
102	0-006	...	103	0-008	...	28	0-009	...	85	0-013	...
16	0-0094	0-019	23	0-017	...	54	0-013	...	21	0-007	0-008
107	0-005	0-009	79	0-007	...	86	0-010	0-0095	84	0-0077	...
103	0-012	...	24	0-013	...	31	0-006	0-005	13	0-085	...
18	0-015	...	55	0-011	...	39	0-013	...	15	0-076	...
73	0-019	0-006	76	0-0098	...	111	0-019	...	14	0-016	...

samples for which these figures are available. Table LXIII. gives the individual oxides by the aqueous iodine method, the figures for MnO being omitted in view of its liability to attack by this method, as shown in the Third Report.

The smallness of the oxide content of pig irons, taken with the

TABLE LXIII.—*Oxides in Pig Irons, Determined by the Aqueous Iodine Method.*

No.	Analysis of Residue.			No.	Analysis of Residue.			No.	Analysis of Residue.		
	SiO ₂ . %.	FeO. %.	Al ₂ O ₃ . %.		SiO ₂ . %.	FeO. %.	Al ₂ O ₃ . %.		SiO ₂ . %.	FeO. %.	Al ₂ O ₃ . %.
69	0-010	0-024	0-003	23	0-012	0-025	0-008	31	0-005	0-011	0-004
70	0-008	0-014	0-002	79	0-005	0-010	0-006	33	0-012	0-016	0-003
68	0-008	0-014	0-003	24	0-010	0-029	0-006	24	0-009	0-035	0-002
65	0-010	0-024	0-002	55	0-010	0-024	0-006	27	0-009	0-013	0-002
64	0-008	0-010	0-002	56	0-007	0-018	0-003	39	0-014	0-014	0-006
101	0-003	0-014	0-002	76	0-007	0-021	0-006	111	0-020	0-023	0-002
38	0-010	0-017	0-004	88	0-013	0-014	0-005	40	0-008	0-013	0-002
102	0-008	0-009	0-002	19	0-008	0-014	0-005	82	0-007	0-036	0-005
16	0-008	0-010	0-006	25	0-008	0-012	0-004	37	0-005	0-032	0-007
107	0-005	0-009	0-003	26	0-007	0-011	0-005	99	0-005	0-012	0-002
109	0-008	0-024	0-004	54	0-009	0-034	0-004	85	0-011	0-023	0-004
103	0-011	0-017	0-002	47	0-011	0-017	0-002	21	0-005	0-015	0-008
18	0-020	0-014	0-004	86	0-005	0-013	0-004	84	0-005	0-013	0-003
73	0-009	0-031	0-003	60	0-015	0-045	Nil	13	0-013	0-279	0-040
35	0-008	0-014	0-005	87	0-007	0-012	0-003	15	0-060	1-110	0-029
50	0-009	0-014	0-002	30	0-007	0-014	0-002	14	0-009	0-037	0-008
75	0-009	0-034	0-002	28	0-008	0-012	0-004	53	0-011	0-038	0-005
108	0-010	0-015	0-003	29	0-009	0-014	0-002				

results of microscopic examination, suggests that a total-oxygen figure will generally be adequate for these materials. Because of this, and on account of uncertainties in the aqueous iodine method,

attention is being devoted to the aluminium reduction and vacuum fusion methods. These uncertainties arise from such possibilities as the partial solution of FeO by the iodine reagent, a low figure for which might be offset by adsorption of iron salts on the surface of the graphite and the carbon liberated by decomposition of the carbides, the variation in distribution of oxides due to heterogeneity of the pig, and the effect of surface oxygen likely to be shown by differences between solid specimens and drillings. Also, reference is made elsewhere in this Report to the work done indicating that the aqueous iodine solution dissolves to some extent both acid and basic oxide-containing slag inclusions. It is, therefore, undesirable at this stage to draw too definite conclusions respecting the aqueous iodine method for the determination of individual oxides in pig and cast irons.

(h) *THE EXAMINATION OF A SERIES OF ALLOY STEELS.*¹

By T. SWINDEN, D.MET. (CHAIRMAN OF THE SUB-COMMITTEE).

SYNOPSIS.

The results obtained by the accepted procedures for the oxygen, hydrogen, nitrogen and non-metallic inclusion contents of a series of alloy steels are given in tabular form. Comments are made and the significance of these results is discussed.

In this sub-section of the Report, the results of a collaborative examination on a series of thirteen alloy steels, comprising most of the well-known types, are given. The work herein described is a continuation of that summarised in Table LVIII. of the Second Sub-Committee Report, 1939, in which the response of the usual oxygen methods to several steels, each with a 0.5% addition of an alloying element, was investigated.

Table LXIV. shows the analyses and a few details of manufacture. A billet from the middle of the selected ingot was rolled to $\frac{7}{16}$ -in. dia. rod and a suitable length was distributed to each co-operating laboratory for examination.

Table LXV. contains a summary of the oxygen results by all methods.

Table LXVI. gives the results of the residue-extraction methods in greater detail.

Table LXVII. contains hydrogen results by both the vacuum-heating and vacuum fusion methods.

Table LXVIII. gives a comparison of the nitrogen contents by the vacuum fusion and chemical distillation methods.

A few brief comments are made on the results shown in Tables LXV. to LXVIII.

¹ Received February 1, 1943.

TABLE LXIV.—Analyses and Manufacture of the Alloy-Steel Series.

Method of manufacture	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.
	Small H.F.; sillimanite lining.			Duplex: Basic O.H.; basic H.F.	Basic H.F.	Basic H.F.	Basic electric arc.	Basic electric arc.	Acid O.H.	Basic electric arc.	Acid O.H.	Acid H.F.	Basic electric arc.
Weight of ingot	18 lb.	18 lb.	18 lb.	14 cwt.	14 cwt.	16 cwt.	14 cwt.	14 cwt.	37 cwt.	6 cwt.	39 cwt.	2½ tons	16 cwt.
Analysis of $\frac{1}{8}$ -in. rod from middle of ingot													
Carbon. %	0.28	0.28½	0.30	0.30	0.18	0.34	0.30	0.29	0.31	0.60	0.33	0.05	1.07
Manganese. %	0.47½	0.45	0.50	0.50	0.44	0.31	0.48	0.51	0.51	0.23	1.40	0.29	13.30
Silicon. %	0.18	0.19	0.25	0.25	0.15	0.12	0.26	0.28	0.27	0.16	0.19	0.39	0.21
Sulphur. %	0.019	0.021	0.049	0.017	0.012	0.012	0.015	0.003	0.051	0.009	0.037	0.024	0.006
Phosphorus. %	0.009	0.010	0.058	0.016	0.016	0.023	0.017	0.008	0.040	0.052	0.041	0.013	0.039
Nickel. %	0.08	0.08	0.007	0.40	0.40½	4.32	3.56	4.32	2.58	0.05	0.38	8.25	0.13
Chromium. %	0.01½	0.00½	0.01	2.98	5.38	12.96	0.74	1.33	0.69	0.11	0.07	18.15	0.07
Molybdenum. %	0.63	0.55½	0.47	...	0.23½
Aluminum. %	0.14½	0.67	0.17	0.04½
Tungsten. %	6.62

(1) *Table LXV. Summary of Total Oxygen Results.*

(a) The oxygen contents obtained by all operators using the vacuum fusion method are in close agreement. With the exception of steel No. 12, the individual results lie within a range $\pm 0.001\%$ of the mean value, although in the majority of these steels the range is much closer. With steel No. 12, the total spread of results is 0.003% of oxygen, but since this steel has the highest oxygen content of the series, the wider range is acceptable. The relatively low oxygen contents of the low-alloy steels, Nos. 4, 5, 7, 8, 9 and 10, and of the high-manganese steel, No. 13, are noteworthy. A certain degree of heterogeneity has been observed with steel No. 1, in which, it is shown later, the bulk of the oxygen exists as alumina.

(b) The fractional vacuum fusion results are in close agreement with the direct total results, and the value on steel No. 13 (13% manganese) has been particularly valuable in assessing the absolute oxygen value of this steel, in view of the potential interference of high manganese contents in the direct total reduction at 1600°C . In this connection, bearing on the high manganese content of steel No. 13, experiments described in Section II., Part A, offer equally confirmatory evidence from another angle.

(c) Both modifications of the aluminium reduction method give results in general agreement with the vacuum fusion method, the agreement being very close in the case of the three aluminium steels, Nos. 1, 2 and 3. With the low-alloy steels, the aluminium reduction method exhibits tendencies towards slightly higher results, whilst with the two high-chromium steels, Nos. 6 and 12, lower oxygen contents are found. It would thus appear that certain oxide compounds in high-chromium steels are not converted to alumina under the conditions of this method. However, with these exceptions, together with steel No. 10, which, being a tungsten steel, necessitated modification to the purely analytical part of this method, agreement with the vacuum fusion method can be said to be satisfactory. Results of 0.010% and 0.0025% of oxygen obtained by Guest Keen Baldwins for steel No. 13 indicate the likelihood of heterogeneity in this sample.

(d) The alcoholic iodine method results on the aluminium steels, Nos. 1, 2 and 3, show satisfactory agreement when the interference introduced by the presence of aluminium and aluminium compounds other than oxide is recognized and suitable modifications are adopted. The results obtained on steels Nos. 7, 8 and 12 must also be considered satisfactory, in view of the complex nature of these steels.

(e) Agreement of the chlorine method on steels Nos. 1, 2 and 3 with the vacuum fusion method is excellent, indicating that the presence of aluminium and/or aluminium compounds introduces no disadvantage to this method. Steel No. 7 shows the influence of chromium on the volatilisation of chlorides at 350°C ., but at

TABLE LXV.—*Summary of the Oxygen Results on the Alloy-Steel Series by All Methods.*

No.	Type of Steel.	Co-operating Laboratory.	Oxygen Content. %.					
			Vacuum Fusion Methods.		Aluminum Reduction Methods.		Residue Methods.	
			Direct Total.	Fractional.	In Hydrogen Atmosphere.	Low Pressure Technique.	Alcoholic Iodine.	Chlorine.
1	0.15% Al	B.F.R.L.	0.009 _s
		C.R.D.	0.009 _s	0.013	...	0.012 _s
		G.K.B.	0.010 _s
		I.O.I.	0.010 _s
		J.L.	0.012 _s	...
		N.P.L.	0.010	0.008 _s	...
		S. & L.	0.010 _s
		Mean value	0.009 _s	0.013	0.010 _s	0.012 _s	0.010 _s	0.010 _s
2	0.5% Al	B.F.R.L.	0.010
		C.R.D.	0.010 _s	0.012 _s	...	0.012
		G.K.B.	0.011
		I.O.I.	0.010
		J.L.	0.013	...
		N.P.L.	0.009 _s	0.012 _s	...
		S. & L.	0.013 _s
		Mean value	0.010	0.012 _s	0.011	0.012	0.012 _s	0.012 _s
3	0.15% Al, 0.01% N ₂	B.F.R.L.	0.008
		C.R.D.	0.009	0.009 _s	...	0.008
		G.K.B.	0.008
		I.O.I.	0.008 _s
		J.L.	0.009	...
		N.P.L.	0.007	0.008 _s	...
		S. & L.	0.011
		Mean value	0.008	0.009 _s	0.008	0.008	0.009	0.010
4	3% Cr, 0.6% Mo	B.F.R.L.	0.002
		C.R.D.	0.002	0.004 _s
		G.K.B.	0.006
		N.P.L.	0.001 _s
		Mean value	0.002	...	0.006	0.004 _s
5	6% Cr, 0.6% Mo	B.F.R.L.	0.004
		C.R.D.	0.005	0.005
		G.K.B.	0.005 _s
		N.P.L.	0.004
		Mean value	0.004 _s	...	0.005 _s	0.005
6	13% Cr	B.F.R.L.	0.008
		C.R.D.	0.009 _s	0.004
		G.K.B.	0.003
		N.P.L.	0.008
		Mean value	0.008 _s	...	0.003	0.004
7	3.5% Ni, 0.7% Cr	B.F.R.L.	0.002
		C.R.D.	0.002	0.005
		G.K.B.	0.003
		I.O.I.	0.003
		J.L.	0.007 _s	...
		N.P.L.	0.001 _s
8	4.5% Ni, 1.25% Cr	Mean value	0.002	...	0.003	0.005	0.007 _s	0.003
		B.F.R.L.	0.003 _s
		C.R.D.	0.004	0.005 _s
		G.K.B.	0.004
		J.L.	0.008 _s	...
		N.P.L.	0.003
		Mean value	0.003 _s	...	0.004	0.005 _s	0.008 _s	...

TABLE LXV.—(Continued.)

No.	Type of Steel.	Co-operating Laboratory.	Oxygen Content. %.					
			Vacuum Fusion Methods.		Aluminium Reduction Methods.		Residue Methods.	
			Direct Total.	Fractional.	In Hydrogen Atmosphere.	Low Pressure Technique.	Alcoholic Iodine.	Chlorine.
9	2.5% Ni, 0.75% Cr, 0.5% Mn	B.F.R.L.	0.003
		C.R.D.	0.003 _s	0.002
		G.K.B.	0.004 _s
		N.P.L.	0.002 _s
		Mean value	0.003	...	0.004 _s	0.002
10	6% W, 0.6% C	B.F.R.L.	0.003 _s
		C.R.D.	0.005 _s	0.004
		G.K.B.	0.008 _s
		N.P.L.	0.003
		Mean value	0.004	...	0.008 _s	0.004
11	1.4% Mn, 0.25% Mo	B.F.R.L.	0.002
		C.R.D.	0.002 _s	0.002 _s
		G.K.B.	0.006
		I.O.I.	0.006
		N.P.L.	0.002
		S. & L.	0.006
		Mean value	0.002	...	0.006	0.002 _s	...	0.006
12	18% Cr, 8% Ni	B.F.R.L.	0.017
		C.R.D.	0.019 _s	0.016	...	0.012
		G.K.B.	0.015 _s
		J.L.	0.026	...
		N.P.L.	0.016 _s	0.023	...
		Mean value	0.017 _s	0.016	0.015 _s	0.012	0.024 _s	...
13	13% Mn, 1% C	B.F.R.L.	0.001
		C.R.D.	0.002	0.001 _s	...	0.002
		G.K.B.	0.002 _s †
		N.P.L.	0.001 _s
		Mean value	0.001 _s	0.001 _s	0.002 _s	0.002

B.F.R.L. = Brown-Firth Research Laboratories, Sheffield.

C.R.D. = Central Research Department, The United Steel Companies, Ltd., Stocksbridge, near Sheffield.

G.K.B. = Guest Keen Baldwins Iron and Steel Co., Ltd., Port Talbot.

I.O.I. = I.O.I. (Alkali), Ltd., Northwich.

J.L. = J. Lysaghts, Ltd., Scunthorpe.

N.P.L. = National Physical Laboratory, Teddington.

S. & L. = Stewarts and Lloyds, Ltd., Corby, Northants.

NOTES: No. 1.—* Results ranging between 0.012_s and 0.008_s% have been obtained.No. 13.—† Results at opposite ends of the sample bar gave values of 0.010 and 0.002_s%.

500° C. reaction is more rapid, separation of the less volatile chromium chloride is more complete and the resulting oxygen value is in excellent agreement with the vacuum fusion result.

(2) Table LXVI. Detailed Analyses of Extracted Residues.

(a) The three aluminium steels, Nos. 1, 2 and 3, have provided very interesting conclusions regarding the recovery of aluminium compounds by residue methods. Whilst the chlorine method appears to separate only alumina, the alcoholic iodine method separates

TABLE LXVI.—*Summary of Non-Metallic Residue Analyses*

No.	Type of Steel.	Co-operating Laboratory. (For Key see Table LXV.)	Method.	Total Ignited Residue. %.	Residue			
					SiO ₂ .		FeO.	
					SiO ₂ . %.	O ₂ . %.	FeO. %.	O ₂ . %.
				5.	6a.	6b.	7a.	7b.
1	0.15% Al	C.R.D.	Fractional vacuum fusion.	...	0.001	0.0006	N.D.	...
		I.C.I.	Chlorine { at 350° C. at 500° C.	0.038 0.029 ₂	N.D. N.D.	...	0.008 0.007	0.0017 0.0016
		J.L.	Alcoholic iodine (boiling method).	0.053 * 0.092 0.070	0.004 0.005 ₂ 0.004	0.0021 0.0029 0.0021	0.009 0.010 0.009	0.0020 0.0022 0.0020
		N.P.L.	Alcoholic iodine (stirring method)	0.063 0.058	0.002 0.001 ₂	0.0010 0.0008	0.006 ₂ 0.007	0.0014 0.0016
		S. & L.	Chlorine, at 350° C.	0.047 0.045	N.D. N.D.	...	0.009 0.008 ₂	0.0020 0.0019
2	0.5% Al	C.R.D.	Fractional vacuum fusion (sample from S. & L.).	...	0.001	0.0004	N.D.	...
		I.C.I.	Chlorine { at 350° C. at 500° C.	0.046 0.028 ₂	N.D. N.D.	...	0.007 0.008	0.0016 0.0018
		J.L.	Alcoholic iodine (boiling method).	0.044 ₂ *	0.003	0.0016	0.007	0.0016
		N.P.L.	Alcoholic iodine (stirring method).	0.078 0.082	0.003 ₂ 0.003 ₂	0.0018 0.0018	0.006 0.007 ₂	0.0013 0.0016
		S. & L.	Chlorine, at 350° C.	0.043 0.041	0.002 0.002	0.0010 0.0010	0.007 0.006 ₂	0.0016 0.0014
3	0.15% Al, 0.01% N ₂	C.R.D.	Fractional vacuum fusion.	...	0.000 ₂	0.0003	N.D.	...
		I.C.I.	Chlorine { at 350° C. at 500° C.	0.035 0.021	N.D. Trace	...	0.006 0.007	0.0014 0.0015
		J.L.	Alcoholic iodine (boiling method).	0.061 * 0.105 0.108	0.005 0.003 0.005	0.0026 0.0016 0.0026	0.011 0.011 0.011	0.0024 0.0024 0.0024
		N.P.L.	Alcoholic iodine (stirring method).	0.097 0.105 0.038	0.002 ₂ 0.003 0.001	0.0013 0.0017 0.0005	0.008 ₂ 0.008 0.007 ₂	0.0019 0.0017 0.0017
		S. & L.	Chlorine, at 350° C.	0.042	0.001	0.0005	0.007 ₂	0.0016
7	3.5% Ni, 0.7% Cr	I.C.I.	Chlorine { at 350° C. at 500° C.	0.022 0.012 ₂	N.D. N.D.	...	0.008 ₂ 0.006 ₂	0.0019 0.0015
		J.L.	Alcoholic iodine (boiling method).	0.056 *	0.008	0.0043	0.006 ₂	0.0015
8	4.5% Ni, 1.25% Cr	J.L.	Alcoholic iodine (boiling method).	0.052 *	0.008	0.0043	0.006 ₂	0.0014
11	1.4% Mn, 0.25% Mo	I.C.I.	Chlorine { at 350° C. at 500° C.	0.055 0.017	0.001 0.001	0.0005 0.0005	0.011 0.003 ₂	0.0025 0.0019
		S. & L.	Chlorine, at 350° C.	0.029 0.046	0.001 0.001	0.0005 0.0005	0.013 0.015 ₂	0.0029 0.0034
12	18% Cr, 8% Ni	C.R.D.	Fractional vacuum fusion.	...	0.008	0.0044	0.002 ₂	0.0005
		J.L.	Alcoholic iodine (boiling method).	0.107* 0.108*	0.030 0.028	0.0160 0.0150	0.007 0.006	0.0016 0.0013
		N.P.L.	Alcoholic iodine (stirring method).	0.098 0.091	0.023 ₂ 0.024 ₂	0.0126 0.0130	0.003 ₂ 0.005	0.0008 0.0011
13	13% Mn, 1% O	C.R.D.	Fractional vacuum fusion.	...	0.001	0.0004	N.D.	...

* * These residues washed with sodium carbonate and hydrochloric acid. Alumina

and Oxygen Results by Residue Extraction Methods.

Analysis Expressed as a Percentage of the Steel.								Total Components as Percentage of Ignited Residue. %.	Total Oxygen Content (Sum of 8b, 7b, 8b, 9b). %.
MnO.		Al ₂ O ₃ .		TiO ₂ . %.	Cr ₂ O ₃ . %.	P ₂ O ₅ . %.	Al ₂ O ₃ Soluble in Sulphuric Acid. %.		
MnO. %.	O ₂ . %.	Al ₂ O ₃ . %.	O ₂ . %.						
8a.	8b.	9a.	9b.	10.	11.	12.		13.	14.
N.D.	...	0-026 _s	0-0012 _s	N.D.	0-013
N.D.	...	0-017 _s	0-0082	...	0-010 _s	0-001 _s	0-010
N.D.	...	0-019 _s	0-0093	...	0-001 _s	0-001 _s	0-011
Trace	...	0-016	0-0075	0-000 _s	0-000 _s	0-004	0-017	97-2	0-011 _s
Trace	...	0-019	0-0089	0-002	0-001	0-005	0-046	96-3	0-014
Trace	...	0-018	0-0085	0-001	0-001	0-004	0-030	98	0-012 _s
Trace	...	0-013 _s	0-0063	Trace	Trace	0-003 _s	0-035	103	0-008 _s
Trace	...	0-012 _s	0-0059	Trace	Trace	0-003 _s	0-033 _s	102	0-008 _s
N.D.	...	0-017 _s	0-0082	N.D.	0-012	0-002 _s	0-010
N.D.	...	0-018	0-0085	N.D.	0-011	0-002	0-010 _s
N.D.	...	0-025	0-0118	0-012 _s
0-002 _s	0-0006	0-016	0-0076	...	0-017 _s	0-001 _s	0-010
0-002 _s	0-0006	0-015 _s	0-0072	...	N.D.	0-001 _s	0-009 _s
0-000 _s	0-0001	0-021	0-0099	0-000 _s	Trace	0-005	0-003 _s	93-0	0-013
0-001 _s	0-0003	0-018	0-0084	...	Trace	0-004	0-041 _s	97-4	0-012
0-001 _s	0-0003	0-020	0-0094	...	Trace	0-002 _s	0-045	98-8	0-013
Trace	...	0-022	0-0104	N.D.	0-006	0-003	0-013
Trace	...	0-024 _s	0-0115	N.D.	0-005 _s	0-002	0-014
N.D.	...	0-019 _s	0-0092	0-009 _s
0-001 _s	0-0003	0-014	0-0066	...	0-010 _s	0-001 _s	0-008 _s
Trace	...	0-013 _s	0-0064	...	N.D.	0-001	0-008
Trace	...	0-010	0-0047	Trace	Trace	0-012	0-019	92-8	0-009 _s
0-001	0-0002	0-009	0-0042	Trace	Trace	0-014	0-065	99	0-008 _s
Trace	...	0-007	0-0033	Trace	Trace	0-020	0-065	101	0-008 _s
Trace	...	0-014	0-0065	...	Trace	0-014 _s	0-056 _s	100	0-009 _s
Trace	...	0-009	0-0041	...	Trace	0-013 _s	0-075 _s	105	0-007 _s
Trace	...	0-018	0-0085	N.D.	0-004	0-006	0-010 _s
Trace	...	0-019	0-0090	N.D.	0-004 _s	0-007	0-011
0-002 _s	0-0005	0-002 _s	0-0012	...	0-004	0-001 _s	0-003 _s
0-002	0-0004	0-002	0-0010	...	N.D.	0-001 _s	0-003
N.D.	...	0-003 _s	0-0016	Trace	0-022	0-014	NiO : Nil	...	0-007 _s
N.D.	...	0-005 _s	0-0026	Trace	0-021	0-009	NiO : Nil	...	0-008 _s
0-001 _s	0-0004	0-006 _s	0-0031	...	0-032	0-001 _s	0-006 _s
0-002	0-0004	0-006	0-0027	...	N.D.	0-001	0-005 _s
Trace	...	0-005 _s	0-0026	N.D.	0-003	0-003	0-006
Trace	...	0-005 _s	0-0026	N.D.	0-016 _s	0-003	0-006 _s
0-007	0-0016	0-019 _s	0-0095	0-016
0-032 _s	0-0073	0-004	0-0019	Trace	0-030	0-003	...	102-7	0-027
0-031 _s	0-0071	0-003	0-0014	Trace	0-033	0-003	...	100	0-025
0-036	0-0081	0-003	0-0014	0-000 _s	0-026	Trace	...	100	0-023
0-034 _s	0-0078	0-002	0-0008	0-001	0-022 _s	Trace	...	101	0-022 _s
0-003	0-0013	N.D.	0-001 _s

found in washings : No. 1, 0-020% ; No. 2, 0-0295% ; No. 3, 0-0505%.

other compounds such as nitrides and possibly, in certain cases, adsorbed aluminium. However, by suitable treatments, the excessive contamination of the alcoholic iodine residues may be removed and both methods yield results comparable with vacuum fusion. The work on these three steels is discussed in detail in Section II. The fractional vacuum results confirm that the oxygen content of these steels exists entirely as alumina, which is interesting, since the aluminium addition was made after the usual silicon and manganese additions.

(b) The alcoholic iodine results on the alloy steels, Nos. 7, 8 and 12, are very satisfactory. The chromium-oxide contamination of the ignited residues of the nickel-chromium steels, Nos. 7 and 8, is small and the high silica results account for the comparatively high calculated oxygen content. The chromium-nickel austenitic steel, No. 12, also shows a small chromium-oxide contamination and a slightly high calculated oxygen content.

(c) The chlorine method has been applied to steels Nos. 7 and 11 with success, the higher chlorination temperature of 500° C. giving the better results in the presence of chromium.

(d) In addition to steels Nos. 1, 2 and 3, the fractional vacuum fusion method has been applied to Nos. 12 and 13. With steel No. 12, whilst the total oxygen content is in agreement with that given by the direct total method, the separation does not compare well with the residue analyses of the alcoholic iodine method, even after making due allowance for the difference in total oxygen contents given by the two methods. The main variation between the results of the two methods lies in the alumina content, and it would appear that separation by fractional vacuum fusion was imperfect in this case. The fractional vacuum fusion result on steel No. 13 shows that the small oxygen content of this steel exists as manganese silicate.

(e) Although the residue examination of this series of alloy steels is very limited, possibilities of the successful application of such methods to alloy steels are apparent and it is hoped that the investigation on these steels will be continued.

(3) *Table LXVII. Hydrogen Contents by the Vacuum Fusion and Vacuum-Heating Methods.*

(a) The hydrogen results in Table LXVII., with the exception of N.P.L. values, are reported to the considered limits of accuracy of each method, viz., 0.5 ml. of hydrogen per 100 g. for the vacuum fusion method and 0.05 ml. per 100 g. for the vacuum-heating method. Owing to an exceptionally low blank, the accuracy of the N.P.L. results is of a higher order of 0.1 ml. per 100 g., and approximation to this limit is adopted in Table LXVII.

(b) The hydrogen contents of these materials, in the form of forged bars, are in general of a low order, i.e., below 1.0 ml. per 100 g.

TABLE LXVII.—*Hydrogen Results on the Alloy-Steel Series by the Vacuum Fusion and Vacuum-Heating Methods.*

No.	Type of Steel.	Co-operating Laboratory. (For Key see Table LXV.)	Hydrogen Content.			
			Vacuum Fusion Method.		Vacuum-Heating Method.	
			%.	Ml. per 100 g.	%.	Ml. per 100 g.
1	0.15% Al	B.F.R.L.	0.00020	2.0	0.000075	0.85
		C.R.D.	0.00005	0.5	0.000030	0.35
		I.C.I.	0.000030	0.35
		N.P.L.	0.00007	0.8
		Mean value	0.00010	1.0	0.000045	0.50
2	0.50% Al	B.F.R.L.	0.00015	1.5	0.000060	0.65
		C.R.D.	0.00005	0.5	0.000030	0.30
		I.C.I.	0.000025	0.30
		N.P.L.	0.00015	1.7
		Mean value	0.00010	1.5	0.000035	0.40
3	0.15% Al, 0.01% N _a	B.F.R.L.	0.00015	1.5	0.000025	0.30
		C.R.D.	0.00005	0.5	0.000030	0.30
		I.C.I.	0.000030	0.30
		N.P.L.	0.00007	0.7
		Mean value	0.00010	1.0	0.000030	0.30
4	3% Cr, 0.6% Mo	B.F.R.L.	0.00010	1.0	0.000060	0.65
		C.R.D.	0.00010	1.0	0.000040	0.40
		I.C.I.	0.000015	0.15 *
		N.P.L.	0.00005	0.5
		Mean value	0.00010	1.0	0.000035	0.40
5	6% Cr, 0.6% Mo	B.F.R.L.	<0.00005	<0.5	0.000045	0.50
		C.R.D.	<0.00005	<0.5	0.000025	0.25
		I.C.I.	0.000015	0.15 *
		N.P.L.	0.00003	0.3
		Mean value	<0.00005	<0.5	0.000030	0.30
6	13% Cr	B.F.R.L.	0.00005	0.5	0.000045	0.50
		C.R.D.	0.00010	1.0	0.000055	0.60
		I.C.I.	0.000020	0.20
		N.P.L.	0.00002	0.2
		Mean value	0.00005	0.5	0.000040	0.45
7	3.5% Ni, 0.7% Cr	B.F.R.L.	<0.00005	<0.5	0.000020	0.25
		C.R.D.	<0.00005	<0.5	0.000040	0.40
		I.C.I.	0.000025	0.25 *
		N.P.L.	0.00001	0.1
		Mean value	<0.00005	<0.5	0.000025	0.30
8	4.5% Ni, 1.25% Cr	B.F.R.L.	0.00010	1.0	0.000025	0.30
		C.R.D.	0.00005	0.5	0.000030	0.35
		I.C.I.	0.000025	0.30 *
		N.P.L.	0.00005	0.5
		Mean value	<0.00005	<0.5	0.000030	0.30
9	2.5% Ni, 0.75% Cr, 0.5% Mo	B.F.R.L.	<0.00005	<0.5	0.000030	0.30
		C.R.D.	<0.00005	<0.5	0.000025	0.30
		I.C.I.	0.000035	0.40
		N.P.L.	0.00002	0.2
		Mean value	<0.00005	<0.5	0.000030	0.35
10	6% W, 0.6% C	B.F.R.L.	0.00010	1.0	0.000035	0.40
		C.R.D.	0.00005	0.5	0.000035	0.40
		I.C.I.	0.000035	0.40
		N.P.L.	0.00004	0.4
		Mean value	0.00005	0.5	0.000035	0.40

TABLE LXVII.—(Continued.)

No.	Type of Steel.	Co-operating Laboratory. (For Key see Table LXV.)	Hydrogen Content.			
			Vacuum Fusion Method.		Vacuum-Heating Method.	
			%.	Ml. per 100 g.	%.	Ml. per 100 g.
11	1.4% Mn, 0.25% Mo	B.F.R.L.	0.00010	1.0	0.000080	0.85
		C.R.D.	0.00005	0.5	0.000025	0.30
		I.C.I.	0.000020	0.20
		N.P.L.	0.00003	0.3
		Mean value	0.00005	0.5	0.000040	0.45
12	18% Cr, 8% N	B.F.R.L.	0.00015	1.5	0.000165	1.85
		C.R.D.	0.00015	1.5	0.000125	1.40
		I.C.I.	0.000115	1.25
		N.P.L.	0.00015	1.7
		Mean value	0.00015	1.5	0.000135	1.50
13	13% Mn, 1% C	B.F.R.L.	0.00020	2.0	0.000200	2.20
		C.R.D.	0.00020	2.5	0.000170	1.90
		I.C.I.	0.000180	2.00
		N.P.L.	0.00025	2.5
		Mean value	0.00020	2.5	0.000185	2.05

* Samples had been heat-treated before the hydrogen determinations to facilitate the preparation of specimens for the chlorine method. The bars were heated at 700° C. for 1 hr., furnace-cooled for 1 hr. and then cooled in air.

Exceptions are provided by the austenitic steels, Nos. 12 and 13, which show hydrogen contents of the order of 2 ml. per 100 g. of steel. The reason for this difference appears to be associated with the difference in permeability to gases of the iron atom in the γ and α states. At equal temperature, the permeability of the γ state is lower than that of the α state, and, consequently, austenitic steels lose hydrogen during manufacture less readily than ferritic steels.

(c) With the exception of the first three steels, agreement by the vacuum fusion method is considered satisfactory, and in regard to steels Nos. 1, 2 and 3 it will be noticed that these were made in the smallest ingot size of the entire series. Consequently, these ingots were subjected to less manipulation during processing to the rod form and possibilities of segregation would be thereby enhanced.

(d) As might be expected, the vacuum-heating method gives closer agreement than the vacuum fusion method, although the effect of the annealing treatment on certain steels (for softening purposes carried out by one co-operator) is apparent in the slightly lower results reported by this laboratory.

(e) Comparison of the two procedures for hydrogen content is best illustrated by steels Nos. 12 and 13, which have the highest hydrogen contents. In each case agreement is very satisfactory.

(4) Table LXVIII. Nitrogen Contents by the Vacuum Fusion and Chemical Distillation Methods.

(a) Considering the vacuum fusion results, agreement between the co-operating laboratories is close, although one or two exceptions

are seen, notably steel No. 5, where the range of results is 0.0035% of nitrogen, and steel No. 13, which shows a wide variation of

TABLE LXVIII.—*Summary of Nitrogen Results in the Alloy-Steel Series by the Vacuum Fusion and Chemical Methods.*

No.	Type of Steel.	Co-operating Laboratory. (For Key see Table LXV.)	Nitrogen. %.	
			Vacuum Fusion Method.	Chemical Method.
1	0.15% Al	B.F.R.L.	0.006	0.005 ₅
		C.R.D.	0.004 ₅	0.006 ₅
		I.C.I.	...	0.007
		N.P.L.	0.005 ₅	0.007
		Mean value	0.005 ₅	0.006 ₅
2	0.5% Al	B.F.R.L.	0.004 ₅	0.004 ₅
		C.R.D.	0.004	0.005
		I.C.I.	...	0.005
		N.P.L.	0.004	0.004
		Mean value	0.004	0.004 ₅
3	0.15% Al, 0.01% N ₂	B.F.R.L.	0.012	0.013 ₅
		C.R.D.	0.009 ₅	0.012 ₅
		I.C.I.	...	0.013
		N.P.L.	0.010	0.010
		Mean value	0.010 ₅	0.012
4	3% Cr, 0.6% Mo	B.F.R.L.	0.010	0.009 ₅
		C.R.D.	0.010 ₅	0.011 ₅
		I.C.I.	...	0.010 ₅
		N.P.L.	0.010 ₅	0.012
		Mean value	0.010 ₅	0.011
5	6% Cr, 0.6% Mo	B.F.R.L.	0.018 ₅	0.018
		C.R.D.	0.019	0.019
		I.C.I.	...	0.020
		N.P.L.	0.015 ₅	0.023
		Mean value	0.017 ₅	0.020
6	13% Cr	B.F.R.L.	0.019	0.019
		C.R.D.	0.017	0.020
		I.C.I.	...	0.020
		N.P.L.	0.020	0.020
		Mean value	0.018 ₅	0.020
7	3.5% Ni, 0.7% Cr	B.F.R.L.	0.010	0.010
		C.R.D.	0.011	0.010 ₅
		I.C.I.	...	0.010
		N.P.L.	0.010	0.012
		Mean value	0.010 ₅	0.010 ₅
8	4.5% Ni, 1.25% Cr	B.F.R.L.	0.010	0.008
		C.R.D.	0.008 ₅	0.012 ₅
		I.C.I.	...	0.007
		N.P.L.	0.010	0.010
		Mean value	0.009 ₅	0.009 ₅

TABLE LXVIII.—(Continued.)

No.	Type of Steel.	Co-operating Laboratory. (For Key see Table LXV.)	Nitrogen. %.	
			Vacuum Fusion Method.	Chemical Method.
9	2.5% Ni, 0.75% Cr, 0.50% Mo	B.F.R.L.	0.004	0.003 ₅
		C.R.D.	0.005 ₅	0.005
		I.C.I.	...	0.004 ₅
		N.P.L.	0.003	0.003
		Mean value	0.004	0.004
10	6% W, 0.6% C	B.F.R.L.	0.007	0.007 ₅
		C.R.D.	0.007	0.006 ₅
		I.C.I.	...	0.006 ₅
		N.P.L.	0.006 ₅	0.007
		Mean value	0.007	0.007
11	1.4% Mn, 0.25% Mo	B.F.R.L.	0.002 ₅	0.004
		C.R.D.	0.005 ₅	0.007
		I.C.I.	...	0.006 ₅
		N.P.L.	0.004	0.007
		Mean value	0.004	0.006
12	18% Cr, 8% Ni	B.F.R.L.	0.012	0.012
		C.R.D.	0.010 ₅	0.014 ₅
		I.C.I.	...	0.015
		N.P.L.	0.011 ₅	0.014
		Mean value	0.011 ₅	0.014
13	13% Mn, 1% C	B.F.R.L.	0.005 ₅	0.010
		C.R.D.	0.011	0.014 ₅
		I.C.I.	...	0.014 ₅
		N.P.L.	0.008	0.011
		Mean value	0.008	0.012 ₅

0.0055%. The latter is of 13% manganese quality and the variability may be connected with the volatility and film formation of manganese or with a nitrogen constituent difficult to decompose.

(b) The chemical nitrogen results have been discussed in detail in Section II., Part C(c), and in the majority of the steels satisfactory agreement has been obtained. Outstanding variations occur in steels Nos. 8, 11 and 13. The variation of chemical results on steel No. 8 as shown in Section II. is a result of the difference in the heat-treated condition and its effect on the usual chemical methods. Steels Nos. 11 and 13 have been the subject of much examination and, as yet, no reason has been found for the two distinct groups of results reported for each steel.

(c) Comparing the results given by both methods, a small but almost constant difference of 0.001–0.0015% of nitrogen is observed, the vacuum fusion result being the lower. Steel No. 13 shows a larger difference of 0.0045% of nitrogen, and further examination of this type of steel is indicated.

Section IV.—The Determination of Oxygen and Hydrogen in Liquid Steel.¹

By T. SWINDEN, D.MET. (CHAIRMAN OF THE SUB-COMMITTEE).

While definite importance attaches to the ultimate oxygen and hydrogen contents of finished steels and it is essential that their determination be accomplished with accuracy, there exists the desirability of making determinations for these two elements during the actual progress of steelmaking operations. The methods described in previous Sections of this Report have now reached a reasonable degree of finality, particularly the vacuum fusion method for total oxygen and hydrogen and the low-temperature extraction method for hydrogen. In the case of oxygen, accurate values for total oxygen in finished sections are obtained either by vacuum fusion or by aluminium reduction, and for certain steels these figures may be further sub-divided into oxygen-bearing constituents, in a more or less accurate manner, by the residue methods or by the fractional modification of the vacuum fusion method. It is doubtful, however, if the evidence presented by these methods can show an appreciable advantage over microscopical examination, except in isolated instances. In any case, both the microscope and analyses of inclusions are "post-mortem" methods and offer no assistance during the actual process of steel manufacture. In regard to hydrogen inferences to be drawn from the figures obtained on fabricated steel by the established methods cannot be regarded as of great significance.

It was shown in the Second Report of the Sub-Committee² that large and small sections (as cast) from the same ladle have different hydrogen contents, and that hydrogen is progressively lowered on standing and with continued working down. It is necessary, therefore, to state the time interval since casting and the thermal history of a section before a true assessment of the significance of the hydrogen value can be made. Also, it is well known that the hydrogen content varies with the position in the section from which the sample was taken, the inside being invariably higher in hydrogen than the outer portions. The position of the sample in the section should, therefore, be stated.

The generally accepted association of hydrogen in steel with hair-line crack formation and the known improvement in mechanical properties of certain steels (notably rail steels) on being allowed to stand in free air—due to gradual diffusion of hydrogen outwards from the steel—appear to indicate that hydrogen in steel is undesirable

¹ Received March 19, 1943.

² Eighth Report on the Heterogeneity of Steel Ingots, Table LX., p. 219, *Iron and Steel Institute*, 1939, *Special Report No. 25*.

and should be kept to a minimum. To this end, in the steelmaking operation, ferro-alloys are roasted, slagmaking materials are carefully dried and so on, to eliminate as far as possible the introduction of moisture to the furnace and the possibility of a hydrogen increase by high-temperature dissociation of water vapour. In part (b) of this Section, Hatfield and Newell describe the methods that they have developed for determining hydrogen in the liquid steel bath and make observations on the behaviour of hydrogen in the presence of certain alloying elements.

The position regarding oxygen in steel is still obscure; whilst high oxygen contents in killed steel are usually associated with undesirable silicate non-metallic matter, often in massive form, it is possible that the *complete* elimination of oxygen would be equally undesirable if it could be achieved in commercial steel manufacture. It is not unlikely that there is an optimum oxygen content for steels of different classes, and this suggestion may possibly have some association with the property of "body," which is often stated to be possessed by certain steels, notably those made from Swedish raw materials. This "residual oxygen" is not believed to have any direct relation to the total oxygen, as determined by the usual vacuum fusion method. On the other hand, it is probably bound up with the low-temperature (FeO-MnO) fraction of the fractional method, as it has its origin in the "oxygen in solution in the steel," which is still remaining after the commercial process of deoxidation has been effected in the furnace, the ladle or the mould. Control of "residual oxygen" and also control of the formation of deoxidation products presuppose an accurate determination of the oxygen content of the steelmaking bath. At the present time, this determination cannot be said to be on an entirely satisfactory basis. Methods are available, depending upon the aluminium-killing of stage samples, with subsequent evaluation, by chemical means, of the alumina formed. It is doubtful, however, if the figures obtained are even of equal value to the steelmaker as are a consideration of "iron in the slag" figures and the rate of carbon removal. The fundamental facts remain that oxygen is the principal refining agent used in steelmaking and that there is meantime no accurate method for its determination *during* the steelmaking process. It is inevitable, therefore, that efforts should continue to be made to solve this problem, and work is going on in certain plants to this end, and Part (a) which follows describes one such investigation.

(a) *THE DETERMINATION OF OXYGEN IN LIQUID STEEL.*¹

By T. SWINDEN, D.MET., AND W. W. STEVENSON, A.I.C.

(Figs. 24 and 25 = Plate XXI.)

SYNOPSIS.

The development of a satisfactory technique for the sampling of liquid steel is described. The sample is taken from the furnace in the form of a small spherical bomb, killed with fine aluminium wire while still in the metal bath.

Three methods of determining the alumina have been investigated and concordant results obtained: (a) Vacuum fusion, (b) gravimetric, (c) nephelometric. The closeness of agreement between the three results suggests that the nephelometric method allied to the bomb-sampling technique forms a suitable basis for the stage laboratory determination of oxygen in liquid steel.

Introduction.

The process of steelmaking is to a large extent governed by the steelmaker's control of oxygen in the liquid steel bath. At the present time, only indirect control is exercised in almost all melting shops, the "state of oxidation of the bath" being judged from "iron in the slag" figures, the rate of carbon removal and other factors emerging from changes in composition of the metal and slag. Temperature control is, of course, of primary importance, and accurate temperature determinations are a necessary corollary to sampling for oxygen values. The immersion couple now being widely used in Britain must be regarded as a most valuable adjunct to this work. There can be no doubt that an experienced steelmaker derives considerable assistance from the indirect data made available by the stage laboratory, but at the same time steelmaking must be regarded at present as an empirical art, dependent upon the experience of the operator in judging the significance of a number of contributory factors. The authors concede immediately that this indirect method of control has been the means of producing a vast tonnage of good-quality steel; they are of the opinion, however, that further real advantages lie in accurate direct knowledge of gases in liquid steel, particularly oxygen, at certain critical stages in steelmaking operations.

The main problem in the determination of oxygen in the liquid steel bath has been found by the authors, after several years of examination of existing methods, to be associated with the sampling of the bath so as to ensure a representative sample being obtained. This sampling difficulty probably interferes to an even greater extent in the determination of hydrogen in liquid steel.

A study has been made of three methods of analytical approach

¹ Communication from The United Steel Companies, Ltd., Central Research Department, Stocksbridge, near Sheffield, received March 19, 1943.

to the determination of oxygen in liquid steel, after having surveyed the sampling problem satisfactorily. These methods have been applied to evaluate the oxygen conversion product, usually alumina, obtained by aluminium-killing the liquid steel; they are:

- (a) Vacuum fusion.
- (b) Gravimetric analysis.
- (c) Nephelometric measurement.

All methods of oxygen determination in liquid steel depend on the "stabilisation" of the oxygen present and its retention in the cold solid sample. Rapid deoxidation by aluminium has been practised for many years in more or less crude forms, and this procedure, with certain refinements, forms the basis of most of the work in this paper. It may be mentioned, however, that certain promise has been given by preliminary experiments on other methods of killing and on rapid quenching.

The recent paper by Derge¹ describes a method of sampling the liquid steel bath in which a small rapidly cooled sample is submitted to vacuum fusion determination. The results obtained are stated to compare favourably with those of the aluminium-killed bomb test. Derge further states that, in his experience, the bomb test is liable to give erroneous results, but the work described below by the present authors does not confirm this conclusion.

The Bomb Method of Sampling for Oxygen in Liquid Steel.

Several years ago the authors made an examination of the Herty² method, which was a development of the original Kichline³ procedure. The analytical procedure for this method requires an hour or more to complete a determination, and it was realised that greater speed must be achieved if the oxygen figure obtained was to be of service on the furnace stage. A modified rapid procedure was described in 1934, in which Kinzel⁴ and his co-workers claimed to have reduced the time of the Herty method to 7-10 min. In their procedure, a spoon sample is taken from the furnace in the usual way and killed by the addition of 1% of aluminium as heavy wire to the test spoon, immediately after the sample is withdrawn from the furnace; the steel is then cast into test moulds. Alternatively, the steel may be poured from the spoon over aluminium wire, with careful blocking of the slag. The test sample is drilled and 5 g. of drillings are dissolved in 250 ml. of 30% nitric acid at 30° C. with

¹ American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1544; *Metals Technology*, Jan., 1943.

² Herty, Freeman and Lightner, U.S. Bureau of Mines, *Report of Investigations* No. 3166, Apr., 1932.

³ Kichline, *Journal of Industrial and Engineering Chemistry*, 1915, vol. 7, p. 806.

⁴ Kinzel, Egan and Price, *Metals and Alloys*, 1934, vol. 5, May, p. 96.

the addition of ammonium persulphate. After solution is complete 15 ml. of hydrochloric acid and 0.05 g. of ashless lamp black (suspended in 20 ml. of water) are added and the solution is centrifuged for 1 min. at 1800 r.p.m. The supernatant liquid is decanted and the residue filtered on double papers with gentle suction. After washing with warm 5% hydrochloric acid, the filter is ignited in platinum in a gentle stream of oxygen and weighed as alumina.

The authors' experience of a large number of results obtained by the above method and by the longer Herty procedure was disappointing, in spite of the fact that many of the samples were taken from very large open-hearth furnaces, which provided an ideal test of the value of the results. These particular furnaces deal only with dephosphorising and decarburising, all alloy additions being made in the ladle. The results obtained appeared to bear no appreciable relation to allied factors, such as the "iron in the slag," the rate of carbon fall, or the loss of manganese in the ladle. It should be noted that bath temperatures were not taken at the time when the work was done and the vacuum fusion method, by which check results may be obtained, was not then in active operation in Britain. There appeared to be definite indications of high results by this method in the low ranges of oxygen content, and indications of low results from highly oxidised baths of very low carbon content. In the light of the higher degree of control at present exercised in the melting plant, as compared with some years ago, it is possible that a re-examination of the Herty method might yield results showing greater correlation with dependent factors—particularly so, if the sampling were improved on the lines described later.

On the occasion of a visit to America, the interest of one of the authors (T.S.) was given an additional incentive by the experience of Dr. Johnston and his colleague, Mr. B. M. Larsen, of United States Steel Corporation. Using a "turbidity" comparison of the alumina deoxidation product, these workers were applying the aluminium-killing procedure with some degree of success. Two methods of sampling were being used, (a) the spoon method, and (b) the bomb method. The former procedure was operated substantially as described earlier for the Kinzel modification of the Herty method; the bomb method consists of taking a sample from the furnace in a sampling device, or bomb, in which the sample is allowed to solidify on withdrawal from the furnace. The bomb consists of two internally hemispherical mild-steel parts, which are slotted and clamped together, forming a spherical container with a small top opening. For sampling, a crumpled ball of aluminium wire occupies the entire volume of the bomb and a tightly fitting metal cap, previously pressed out to the correct shape, covers the top opening of the bomb. The clamp forms the end of the long rod used to insert the bomb in the furnace.

Although a slight preference for the spoon method was professed by the American workers, it is at once apparent that the bomb

method offers three advantages over the spoon method, owing to the fact that no pouring is done :

- (1) Danger of atmospheric oxidation reduced to a minimum.
- (2) Less likelihood of slag contamination.
- (3) Less danger of losing alumina by flotation.

The authors have now carried out numerous determinations of oxygen in liquid steel by the bomb method, using two procedures to determine the alumina :

- (1) A turbidity procedure similar to that used by Johnston.
- (2) A gravimetric determination, as in the Hertzy method.

In many cases, samples have also been subjected to vacuum fusion determination of oxygen and it has thus been possible to check the

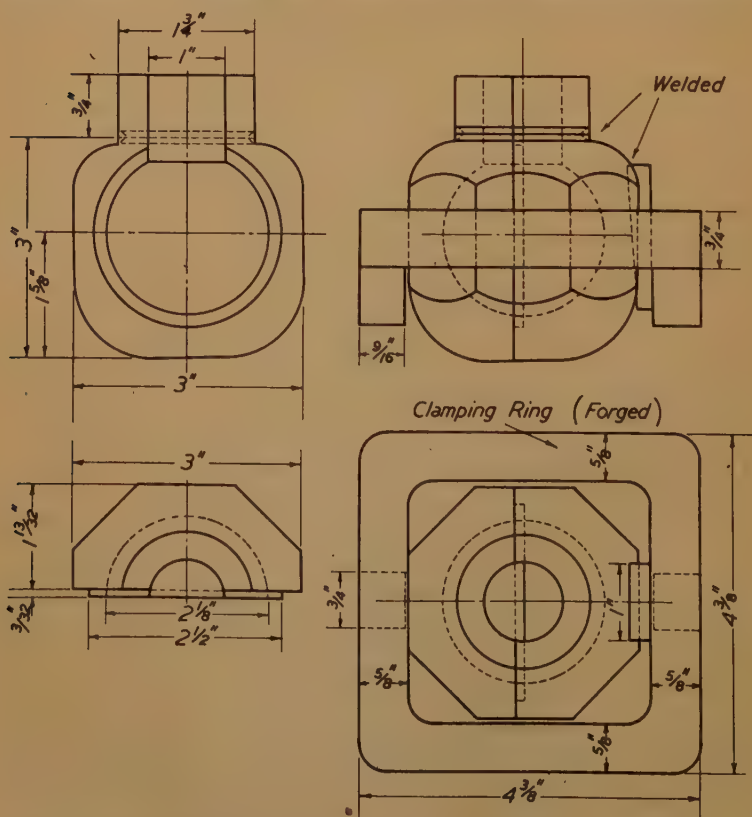


FIG. 19.—Sectional Diagram of Bomb Mould and Clamping Ring used for sampling the liquid steel bath.

validity of the chemical alumina determinations. In this way, the degree of heterogeneity of the actual bomb samples has also been ascertained.

The detailed procedure now adopted by the authors is as follows.

The Bomb-Sampling Device.

A sectional drawing of the bomb and clamping ring is shown in Fig. 19, and the photograph (Fig. 24) illustrates the two halves of the

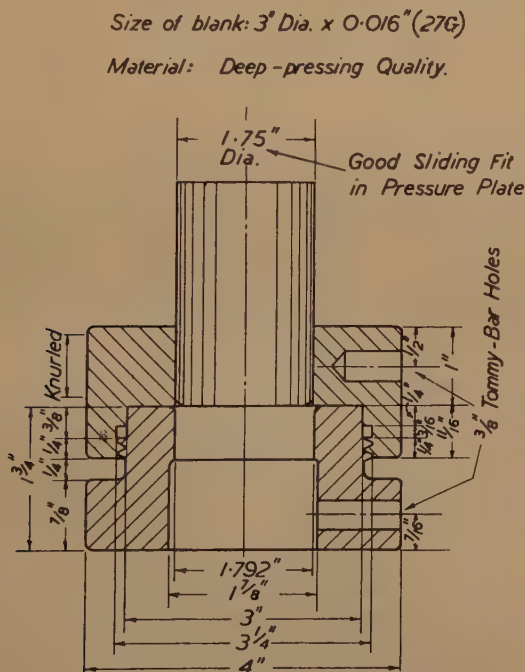


FIG. 20.—Sectional Diagram of Tool used for pressing the covering cap for the bomb mould.

split bomb mould, indicating clearly the central recessed annuli. It is a convenient, if tedious, procedure to machine the bomb parts from mild steel; alternatively, they may be produced more rapidly as hematite-iron castings (as shown in Fig. 24), requiring only finish-machining. In the latter case, it is found that, while the main body of the bomb withstands the severity of the sampling operation, the collar tends to be melted away, rendering difficult the close fitting of the cap. This difficulty is conveniently overcome by replacing the collar with one of heat-resisting steel, welded to the iron bomb. This is indicated in Fig. 19.

Some American workers have used a cap of aluminium sheet to cover the central top opening of the bomb, but the authors found this impracticable in the early stages of their work on 80-ton fixed open-hearth furnaces. The aluminium cap was melted long before the bomb reached the steel bath and it was found impossible to avoid slag contamination. A satisfactory cap is pressed out of 27-gauge (0.016-in.) deep-pressing-quality mild steel sheet, and when in position on the bomb it covers the top opening and the collar. One of these caps is illustrated in Fig. 24 and the tool for preparing them is shown in Fig. 20.

Taking the Bomb Sample.

A crumpled ball, consisting of 5 g. of 30-gauge aluminium wire, is placed in position between the two halves of the bomb mould, so that when they are clamped together in the clamping ring the spherical volume of the bomb is almost entirely occupied by the wire. The cap is then placed in position. The bomb is carefully slagged, almost up to the top of the cap, and is rapidly plunged through the slag below the metal surface. This is best accomplished by balancing the rod (carrying the clamping ring) on the sill below the furnace door, as it is found that the bomb is full of metal when the rod commences to be overbalanced. It is essential that the bomb be full of metal to avoid slag contamination; on the other hand, the bomb should not stay in the bath longer than is necessary to fill it completely. Under the conditions of fixed basic open-hearth furnaces of 80 tons capacity, in which most of the authors' work has been done, the time required for filling the bomb is of the order of 9–12 sec.¹

Analysis of the Bomb Sample.

On removal of the clamping ring, the two halves of the bomb mould fall apart, revealing a sample of the shape illustrated in the top left corner of Fig. 25. Other sections in this photograph illustrate the effect of using 10 g. (double the usual amount) of aluminium wire (top centre) and insufficient time in the furnace (top right). In the latter sample, unmelted aluminium wire can be seen clearly on top of the solidified steel.

The bomb sample is drilled for the chemical analysis of alumina, or is forged down to 0.4-in. dia. bar for the preparation of specimens for vacuum fusion determination. The relative sizes of the as-forged bar (centre right) and sectioned bomb samples are shown in Fig. 25.

¹ Comparatively recent work on the bomb method in large tilting furnaces by Dr. Reeve, of the Appleby-Frodingham Steel Company, Ltd., indicates that an entirely different technique is required in this type of furnace, with its wider sill, greater bath area, deeper slag covering, &c.

Gravimetric Determination of the Alumina.

Dissolve 10 g. of drillings in 50 ml. of hydrochloric acid (sp. gr. 1.16) and digest until solution is complete. Dilute with an equal volume of water and filter through a paper pulp pad, washing with hot hydrochloric acid solution (1 : 1) and cold water. Ignite in a weighed platinum crucible, treat the residue with hydrofluoric acid and re-ignite. The increase in weight of the platinum crucible, after correction for a blank due to filter-pad ash, &c., is converted to an equivalent oxygen percentage.

The residue may be fused with either sodium carbonate or potassium bisulphate and the alumina content obtained by conventional methods.

Nephelometric Determination of Alumina.

Dissolve 2 g. of drillings in 30 ml. of the following mixture :

30 ml. of orthophosphoric acid (85%).
90 ml. of nitric acid (sp. gr. 1.42).
80 ml. of water.

Boil for 3 min., add 10 ml. of ammonium persulphate solution (10%) and continue boiling for a further 3 min. Cool to room temperature and dilute to 50 ml. with nitric acid solution (2%). After mixing, transfer the solution to a 5-cm. cell and measure the light absorption in the Zeiss Pulfrich photometer, using the red filters Nos. 6 or 7, with water as comparison liquid.¹ The oxygen content of the sample is then obtained by reference to a calibration chart connecting the extinction coefficient with the oxygen content.

Any of the well-known types of colorimeter may be used for the turbidity comparison, and in the absence of such an instrument reasonable results, of a lower degree of accuracy, may be expected from visual colour comparison, using turbidity standards.

Vacuum Fusion Determination of Total Oxygen.

After machining suitable-sized specimens from the 0.4-in. dia. bar forged from the bomb sample, total oxygen determinations are carried out by the procedure described by Stevenson and Speight.²

Evaluation of the Bomb Sample.

In regard to the possibility of heterogeneity in the bomb samples themselves, drillings were taken with a $\frac{1}{4}$ -in. drill at eight points in the cross-section, as shown in Fig. 25 (centre, left) and the diagram Fig.

¹ It should be noted that water is a satisfactory comparison liquid for steels substantially free from alloying elements. In the presence of the latter, a portion of the solution should be filtered and the clear filtrate used as the comparison liquid.

² Seventh Report on the Heterogeneity of Steel Ingots, p. 65, *Iron and Steel Institute*, 1937, *Special Report No. 16*.

21. The results obtained (by the nephelometric method) are given in Table LXIX. In terms of oxygen percentage as determined by the gravimetric alumina method, the highest and lowest values quoted in Table LXIX. represent 0.0183% and 0.0175%, respectively.

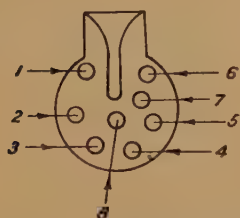


FIG. 21.—Drilling Positions for Evaluation of Bomb Sample Heterogeneity.

TABLE LXIX.—Bomb Sample Heterogeneity (Nephelometric Method).

Position.	Extinction Coefficient <i>E</i> .
1	0.642
2	0.619
3	0.620
4	0.616
5	0.618
6	0.619
7	0.617
8	0.616

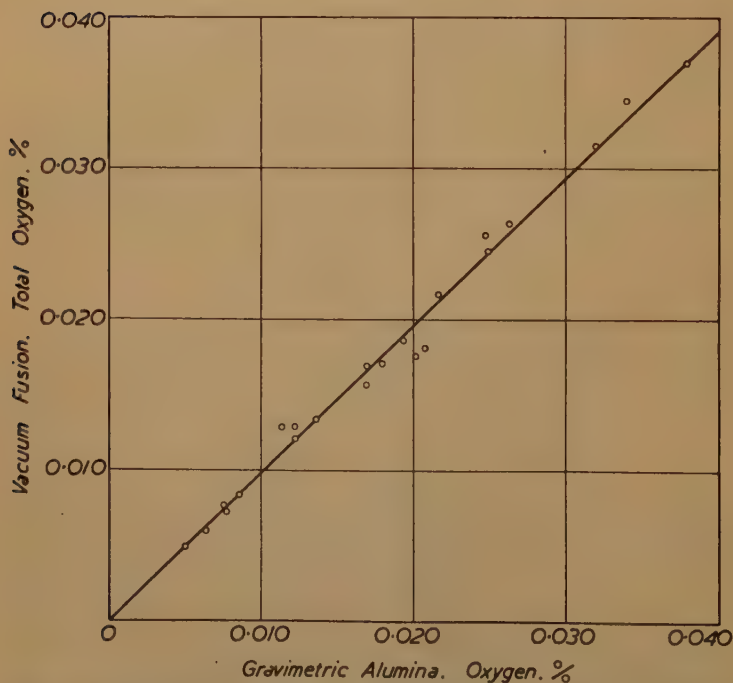


FIG. 22.—Oxygen in Liquid Steel. Calibration curve of vacuum fusion and gravimetric alumina results on bomb samples.

Similar exploration was made of other bomb samples, and the consistent results reported above were, in every case, repeated. It was evident, therefore, that the bomb may be drilled at any point in the lower half and representative results for oxygen content be obtained. Similarly, in regard to vacuum fusion specimens, forging the bomb sample from the lower end provides an ample length of bar from which satisfactory samples may be machined.

Consideration of the Results Obtained.

The vacuum fusion total-oxygen figures have been used as a means of assessing the values obtained by the gravimetric and nephelometric procedures.

A number of bomb samples were taken at various stages of basic open-hearth practice, from melted to tapping, and the figures given in Table LXX. are results obtained by the three analytical methods previously described. Fig. 22 gives a comparison between the vacuum fusion total-oxygen and the gravimetric alumina value, while the relation between the vacuum fusion total-oxygen and the nephelometric value is indicated in Fig. 23. The two curves indicate

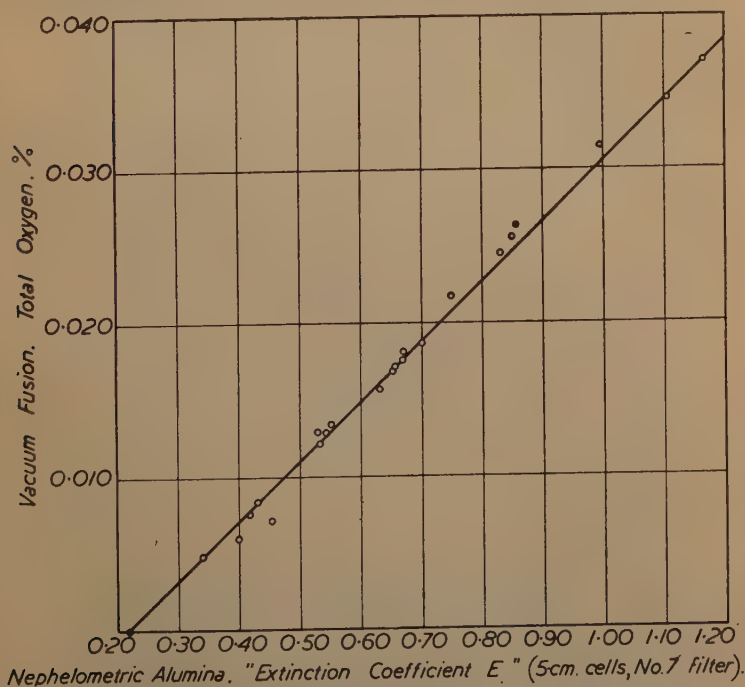


FIG. 23.—Oxygen in Liquid Steel. Calibration curve of vacuum fusion and nephelometric alumina results on bomb samples.

the close agreement which has been obtained, and the authors are of the opinion that the direct determination of oxygen in liquid steel is a definite possibility, on the lines indicated in the foregoing.

The time required for the nephelometric method—from with-

TABLE LXX.—*Results on Basic Open-Hearth Bomb Samples, obtained by Vacuum Fusion, Gravimetric Alumina and Nephelometric Alumina Methods.*

Cast No.	Sample No.	Bath Carbon. %.	Vacuum Fusion. Total Oxygen. %.	Gravimetric Alumina. Oxygen. %.	Nephelometric Alumina. Extinction Coefficient E. ¹
34/2238	1	0.44	0.0076	0.0075	0.417
	2	0.13	0.0245	0.0249	0.830
	3	0.14	0.0263	0.0263	0.855
30/4600	1	0.65	0.0134	0.0136	0.550
	2	0.22	0.0157	0.0169	0.632
31/501	1	0.15	0.0186	0.0193	0.699
	2	0.17	0.0176	0.0201	0.668
31/508	1	0.33	0.0084	0.0085	0.431
	2	0.19	0.0169	0.0169	0.653
	3	0.19	0.0181	0.0207	0.669
35/7148	1	0.42	0.0072	0.0077	0.452
	2	0.26	0.0129	0.0122	0.542 _s
35/7156		0.29	0.0121	0.0122	0.533
31/599		0.48	0.0060	0.0063	0.400 _s
31/572	1	0.23	0.0129	0.0113	0.529
	2	0.15	0.0256	0.0247	0.851
30/4591	1	0.80	0.0049	0.0050	0.340
	2	0.24	0.0217	0.0216	0.750
	3	0.27	0.0171	0.0179	0.656
36/5453		0.20	0.0315	0.032	0.994
27/5679		0.12	0.0345	0.034	1.104
35/6847		0.12	0.037	0.038	1.166
	Blank	0.219

¹ Solution filtered twice and compared with water in obtaining the blank for the nephelometric alumina method. 5-cm. cells, No. 7 filter used.

drawing the bomb sample from the furnace to the reporting of the result—is of the order of 20 min.

The gravimetric procedure, using rapid modifications on the lines of Kinzel and his co-workers (*loc. cit.*), occupies a little longer—25–30 min. It is suggested, therefore, that a reliable oxygen figure



FIG. 24.—Two Halves of Bomb Mould, as cast in hematite iron, together with pressed-steel cap for covering the top opening of the mould.

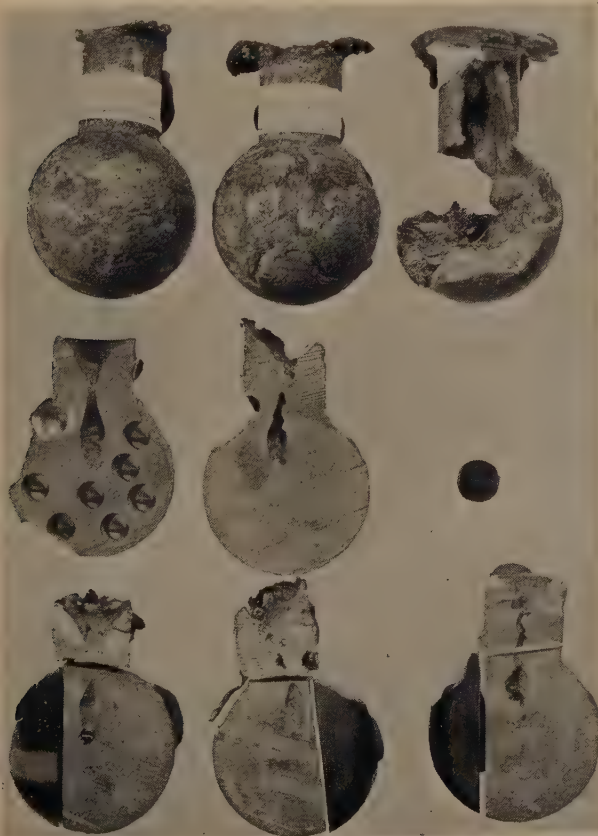


FIG. 25.—Bomb Samples as obtained and after Sectioning, showing also relative sizes of bomb section and vacuum fusion bar forged from the bomb sample.

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[To face p. 406 P.



FIG. 26.—Split Mould for Sampling Liquid Steel and Test-Piece.

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[Section IV.(b).

[To face p. 407 P.

may be obtained sufficiently rapidly to be of value on the melting-shop stage.

This Sub-Committee is concerned primarily with methods of analysis; hence, it is not within the scope of this paper to discuss the significance of individual results obtained for oxygen in liquid steel. It is perhaps not irrelevant, however, to indicate results obtained in the casting pit in making rimming steel. For this purpose a modification of the bomb method was employed, in which the stream of metal from the ladle is allowed to run at fair speed into a sampling mould filled with the 30-gauge aluminium wire. The mould is tilted at an angle of 45° while receiving the molten metal. The results given in Table LXXI. were obtained by all three methods on pit samples taken while teeming four casts of rimming steel.

TABLE LXXI.—*Oxygen Contents of Pit Samples Obtained While Casting Rimming Steel.*

Cast No.	Vacuum Fusion. Total Oxygen. %.	Gravimetric Alumina. Oxygen. %.	Nephelometric Alumina. Oxygen. %.
29/9106	0.031	0.034	0.034
35/7407	0.019	0.020	0.022
30/4918	0.017	0.019	0.018
27/6293	0.032	0.033	0.034

It may be pointed out that, for the purpose of establishing satisfactory methods, the work described in this paper has been carried out almost entirely on carbon steel, made by the basic open-hearth process. However, it is perhaps for this type of steelmaking process that fundamental knowledge and rapid, direct methods of oxygen determination in liquid steel are most desirable.

The authors acknowledge the valuable assistance of Mr. Y. K. Zea, B.Sc., in taking many of the bomb samples and carrying out gravimetric and nephelometric alumina determinations on the samples. Also their thanks are due to the Directors of The United Steel Companies, Ltd., for the necessary permission for publication.

(b) *THE DETERMINATION OF HYDROGEN IN LIQUID STEEL.*¹

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(Fig. 26 = Plate XXII.)

SYNOPSIS.

A detailed account is given of the methods used in the Brown-Firth Research Laboratories for the determination of the hydrogen content of molten steel. Small samples are collected in chill-moulds, and their hydrogen content is determined as rapidly as possible

¹ Received March 19, 1943.

afterwards by the vacuum fusion method previously described. In the balloon-tube method the gas given off during solidification and cooling is also collected under atmospheric pressure and analysed. Such gas evolved is added to that found in the solid samples to give the actual gas content of the liquid steel. The relation between the hydrogen content of the liquid steel and the residual hydrogen content of the solid metal is considered important. A series of results for steels of different qualities is given, and deductions are made as to the effect of alloying elements upon the presence of hydrogen in liquid and solid steel. Briefly, these are that chromium increases the amount of hydrogen found in liquid steel under commercial conditions as well as that retained in rapidly chilled solid steel. Nickel steel with up to 4% of nickel does not seem capable of retaining more hydrogen in the rapidly chilled solid condition than would plain carbon steel in the same condition.

The sampling of liquid steel for its hydrogen content is a very much more difficult problem than sampling for its oxygen content. Hydrogen is the most volatile of all substances, and there are no known means whereby hydrogen can be fixed at very high temperatures in any stable chemical compound, in any analogous manner to the retention of oxygen as alumina by interaction with metallic aluminium. There is also the difficulty of finding a refractory which will resist the action of metal and slag and at the same time be impervious to hydrogen. Any successful method for the determination of hydrogen in molten steel must overcome the difficulties introduced by these factors.

Most investigators have used evacuated containers for the collection of liquid steel samples so as to avoid atmospheric oxidation. The vacuum, in conjunction with a deoxidant, such as aluminium, doubtless helps to give a more reliable figure for the oxygen content of molten steel, but for hydrogen determination the authors have found that a vacuum merely increases the quantity of hydrogen evolved from the metal and adds to the uncertainty as to the quantity of metal associated with that evolved gas. The methods used for hydrogen estimation on the molten steel are, in general, applicable to oxygen estimation also. The converse, however, does not apply, and this paper deals only with that specialised technique that the authors have developed for estimating the hydrogen contents of the molten metal.

The principle employed in the authors' sampling methods is to chill a sample of the molten metal as rapidly as possible under conditions in which the loss of hydrogen during solidification and cooling down is hindered and estimated. Actually, two distinct methods have been employed, the one being a relatively simple method of casting a small notched pencil test-piece in a thick-walled chill mould and neglecting any hydrogen evolved, and the other being a more elaborate method in which a small test-piece is frozen in a thick-walled tube and any hydrogen evolved is collected and measured. It will be seen that the former method tends to give low hydrogen results.

The Notched Chill-Mould Method.

If it is assumed that the hydrogen content of the solid cast steel bears any relationship to the hydrogen content of the molten metal before casting, then it should be possible to determine the hydrogen content of the solid metal and to use the figure obtained as a guide to the hydrogen content of the molten metal. The authors decided, therefore, to collect samples in a carbometer test mould, which would chill the metal very rapidly, and to transfer the sample to the vacuum fusion apparatus as quickly as possible. It was soon found that the samples prepared in this manner were in such a hardened state, by virtue of their rapid chilling, that machining of suitable specimens took far too long and tended to heat the pieces too much, which is undesirable—bearing in mind that there is good evidence that hydrogen is very easily lost even at only a moderately elevated temperature. To break off the specimens was rather an uncertain operation, so it was then decided to prepare a modified carbometer test-piece, $\frac{1}{2}$ in. in dia., having a series of annular grooves or notches, so spaced that suitable specimens were easily snapped off from the chill-cast test-pieces. Fig. 26 is a photograph of the split mould which was designed for the purpose and of a sample taken therein. In this mould the test-piece is chilled even more effectively than in the carbometer test mould.

The procedure for sampling is to take a spoonful of molten steel from the furnace, and then, having skimmed off any slag, to pour the metal into the clamped split mould. Solidification takes place within a second, the test-piece is removed, and specimens are broken off therefrom, being vacuum-melted and extracted as soon as possible.

The Balloon-Tube Method.

This method was evolved after a consideration of the work of others who had attempted to withdraw samples of molten steel into tubes. Wüster and Piowowsky¹ used an evacuated tube, sealed at its lower end with a fusible seal, and found considerable quantities of carbon monoxide, carbon dioxide, hydrogen, methane and nitrogen. Hare, Peterson and Soler,² using a somewhat simpler and more easily portable apparatus on the same principle, found that the evolved gas consisted of hydrogen and carbon monoxide with only traces of other gases. Herasymenko and Dombrowsky³ use a simpler method, in which a small quantity of steel is cast into a vessel which is subsequently covered and vacuum-extracted. These authors also use the method of Hare and his collaborators, and show that both methods agree as to the amounts of hydrogen which they

¹ Wüster and Piowowsky, *Stahl und Eisen*, 1927, vol. 47, p. 698.

² Hare, Peterson and Soler, *Transactions of the American Society for Metals*, 1937, vol. 25, p. 889.

³ Herasymenko and Dombrowsky, *Archiv für das Eisenhüttenwesen*, 1940, vol. 14, p. 109.

indicate to be present in the molten steel. They also admit that theoretically the sampling according to Hare, provided that the hydrogen remaining in the solid steel is also taken into account, appears to be the better of the two, though its disadvantage is the relatively large dimensions of the apparatus. The authors agree with Herasymenko and Dombrowsky's opinion as to the relative merits of the two methods, and before their publication in 1940 had devised the balloon-tube method as a modification of the Hare method.

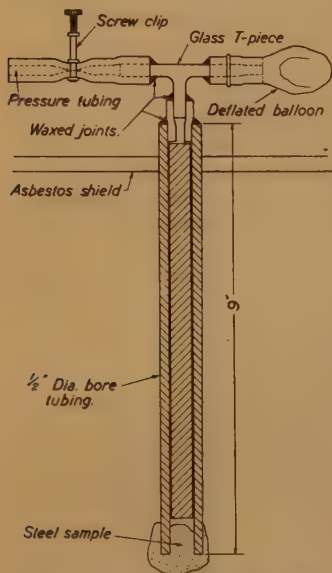


FIG. 27.—The Balloon-Tube Method of Sampling Liquid Steel.

The essential principle of the method is that a small sample of molten steel is rapidly frozen and isolated under a pressure of one atmosphere of gas, the pressure being maintained constant throughout the sampling period until the sample is cold. The manner in which this is performed will be seen in Fig. 27, which shows a section of the apparatus with a sample of steel collected on its lower end. A piece of thick-walled high-pressure hydraulic tubing, 9 in. long and $\frac{1}{2}$ in. in bore, is thoroughly cleaned internally, after which one end is tinned, washed free from flux and dried at 150°C . for an hour. A piece of clean tinned copper foil is then sealed over the tinned end of the tube by the application of heat only, so as to avoid any possibility of the introduction into the tube of any traces of water

or moisture-containing fluxes. The bulk of the space in the tube is then filled with a length of clean steel rod, which fits sufficiently tightly not to fall out and yet which allows of a free flow of gas between itself and the tube. The upper end of the tube is then fitted to a small glass T-piece, which also connects *via* thick rubber tubing to a small toy balloon and to another piece of rubber tubing fitted with a screw clip. Before use the tube is evacuated by opening the screw clip and by connection to a rotary oil pump and tested for vacuum-tightness. It is then evacuated and washed out with dry nitrogen alternately three times, finally being filled up with the nitrogen to a pressure of about 1 in. of mercury below atmospheric pressure. The nitrogen is prepared directly from the air by drawing air through a series of three alkaline hydrosulphite bubblers, followed by one alkaline pyrogallol bubbler (for observation of exhaustion of

the hydrosulphite) and about 2 m. length of glass tubing filled with silica gel to dry the nitrogen. The whole of the gas train is stored in a portable wooden box, and it has been found a very satisfactory means of supplying small quantities of dry nitrogen. The pressure of nitrogen obtained is automatically less than atmospheric pressure by an amount determined by the series of bubblers.

A series of such steel tubes is prepared just before they are required, and they are used in the following manner: A spoonful of molten steel is taken from the furnace in a previously slagged spoon, and the lower end of the tube is immersed in the slag-skimmed steel to a depth of about 1 in., the balloon being protected from the intense radiation by means of a sheet of asbestos just above the tongs used for holding the tube. Depending somewhat upon the superheat of the steel, but generally after about 4 sec., the tube is slowly withdrawn from the spoon, after which it is allowed to cool and is taken to the laboratory for extraction of the gas and vacuum fusion of the solid sample within the tube. What happens is that the balloon, which is previously flattened and deflated, receives the gas given off by the steel, while still remaining under essentially atmospheric pressure so long as the rubber of the balloon is not stretched, a condition which is always maintained. By the time the copper-foil seal has melted, the nitrogen within the tube has been warmed sufficiently for its pressure to have risen to that of the external atmosphere, so that the steel rises in the tube to the same extent as the tube is immersed in the molten steel.

One of the great advantages of collecting the sample under atmospheric pressure is that, should the steel not seal around the end of the tube perfectly—as is often the case—then the tendency for loss of gas or pick-up of air is a minimum. As a safeguard it is the authors' practice to immerse the lower end of the tube, when it is cold and with its steel sample attached, in a beaker of water before removing the gas sample from the tube. Under these conditions, should there be a leak between the steel sample and the tube, on drawing the gas sample up into the gas-analysis apparatus the gas is displaced by water and not air, and there is thus no dilution of the gas sample.

The gas collected from the tube is found to consist of the nitrogen originally put in the tube (about 5 ml.) plus the hydrogen evolved from the steel (up to 1 ml.), together with some carbon monoxide, especially from wild steel samples. Oxygen from the atmosphere can be present in appreciable quantities if the steel does not seal the end of the tube properly, but carbon dioxide and methane have not been detected. Since hydrogen has been the primary concern in this research, and speed in dealing with the samples is essential, it is now the authors' practice to eliminate oxygen and carbon monoxide together by means of ammoniacal cuprous chloride, and to reject the gas after explosion with added oxygen.

The solid steel sample is removed from the end of the tube by

first loosening the sample by hammering and then pushing the sample out by means of a rod passed down the tube. Occasionally the steel welds itself to the tube, in which case the sample and the end of the tube must be machined. As a general rule the steel tubes can be used over and over again for the collection of samples. The size of the tube is so chosen that the sample collected within it is of the form of a cylinder, 0.5 in. in dia. and about 0.5 in. in length, so that it is immediately ready for insertion in the vacuum fusion apparatus. In any such method of sampling molten metal there is bound to be some doubt as to the weight of metal to be associated with the evolved gas. That was one reason why the authors endeavoured to retain as much gas as possible in the solid metal, so that the evolved gas would be only a corrective factor to that obtained from the solid metal. In calculating the results the reasonable assumption was made that the gas evolved in the tube was that which had come off from the steel that had entered the tube.

It was feared that hydrogen might be lost by diffusion through the rubber of the balloon, but this fear proved groundless under the conditions of the experiments. To test this point a measured quantity of coal-gas was allowed to pass into a previously evacuated balloon, so that it was filled without stretching the rubber. After a period of about 2 hr. the gas was withdrawn, and it was found that there had been no appreciable loss of gas. Since the authors' gas samples were in the balloons for a matter of only a few minutes, the possibility of error by loss of hydrogen through the balloon is thus eliminated.

All of the results detailed in this paper are for molten steel samples taken in a spoon from basic electric melts. It would seem possible that hydrogen could be lost during the operation of removing the spoonful of metal from the furnace or ladle, and the authors are therefore endeavouring to apply the balloon-tube method to sampling direct from the furnace or ladle. For this purpose the rubber balloon and all the glass and rubber connections are well covered with a thick layer of asbestos wool and sheet, and the tube is clamped at one end of a 12-ft. length of light-weight steel tubing, which acts as a supporting arm and by the aid of which the sampling tube is dipped into the molten steel in a ladle. The presence of slag is the major difficulty in this type of sampling.

Results obtained by Both Methods, and Conclusions.

In Table LXXII. are a series of results for the hydrogen content of molten steel of various qualities and during various stages of the melting operation. Comparison tests were taken at approximately the same time by both the notched chill-mould and balloon-tube methods. Attention was concentrated upon hydrogen contents only, and no attempt was made to determine oxygen simultaneously, as this would have necessitated the careful grinding-off of the high-

TABLE LXXII.—Hydrogen Content of Molten Steel in Relation to the Hydrogen Retained after Solidification and Cooling.

Cast No.	Analysis of Steel.				Condition of Bath.	Hydrogen. %.			
	Analysis of Steel.					Balloon-Tube Test.			Chill-Cast Pencil Test.
	C. %.	Cr. %.	Ni. %.	Other Elements. %.		In Solid Metal.	Evolved.	Total in Liquid Steel.	
84,504	0.07	After boil.	0.00060	< 0.00005	0.00060	0.00030
84,658	0.08	After boil.	0.00065	0.00050	0.00115	0.00025
84,944	0.16	Just before tapping.	0.00030	< 0.00005	0.00030	0.00025
84,770	0.27	...	2.4	0.2 V	Just before tapping.	0.00010	< 0.00005	0.00010	0.00005
84,559	0.08	0.13	1.8	0.20 Mo	Just before finishings.	0.00045	< 0.00005	0.00045	0.00020
					Repeat test.	0.00045	< 0.00005	0.00045	...
84,434	0.36	0.17	3.3	...	Just before tapping.	0.00055	0.00020	0.00075	0.00040
84,932	0.05	0.25	2.5	...	After melting down.	0.00025	< 0.00005	0.00030	0.00020
84,776	0.10	0.26	2.3	0.41 Mo	During boil.	0.00025	< 0.00005	0.00025	0.00025
84,501	0.18	0.47	3.1	...	Just before finishings.	0.00030	0.00005	0.00030	0.00020
84,774	0.30	0.72	2.8	0.48 Mo	Just before tapping.	0.00010	0.00040	0.00050	0.00015
84,399	0.52	0.82	1.7	0.34 Mo	Just before tapping.	0.00030	0.00005	0.00035	0.00030
					Repeat test.	0.00040	< 0.00005	0.00040	...
84,436	0.14	1.06	3.4	...	Just before tapping.	0.00055	< 0.00005	0.00055	0.00035
84,656	0.42	1.20	1.6	0.38 Mo	Just before tapping.	0.00035	0.00080	0.00115	0.00020
84,946	0.15	1.23	4.3	...	Just before tapping.	0.00050	< 0.00005	0.00050	0.00025
84,655	1.45	1.60	0.5	...	Just before tapping.	0.00045	< 0.00005	0.00045	0.00040
84,540	0.44	1.65	0.3	0.23 Mo	Just before tapping.	0.00065	< 0.00005	0.00065	0.00055
84,566	0.11	5.60	2.5	...	After removing bulk of slag.	0.00070	0.00005	0.00075	0.00045
84,146	0.13	11.2	0.3	...	After removing bulk of slag.	0.00095	0.00020	0.00115	0.00095
					After melting down.	0.00085	0.00055	0.00140	0.00085
83,570	0.15	17.1	2.5	...	Just before tapping.	0.00110	0.00030	0.00140	0.00090
84,689	0.15	18.5	9.9	...	Just before tapping.	0.00070	< 0.00005	0.00070	0.00070

temperature oxide from the samples, a procedure which would have caused considerable delay in the examination of the samples. Most of the samples were taken when the molten steel in the furnace was in a quiet condition, *i.e.*, boiling periods were usually avoided, and the results were not complicated by the addition of any deoxidant to the spoonful of metal withdrawn from the furnace.

In general, the hydrogen content of the solid balloon-tube sample is higher than that of the chill-mould pencil sample. When the hydrogen collected in the balloon is added to that found in the solid sample, the resulting figure may reasonably be considered to represent the hydrogen content of the molten steel; it is generally substantially higher than that of the chill-mould pencil sample. Duplicate tests taken at the same time show that, whilst the hydrogen evolved during solidification and cooling is variable, the total hydrogen attributed to the molten metal is reasonably consistent. The large differences between the hydrogen found in the solid balloon-tube sample and in the pencil sample, as well as the variability of the evolved hydrogen, show how dependent upon the effectiveness of the chilling of the metal is the residual hydrogen left in the solid metal. In many cases the hydrogen content of the pencil sample is a guide to the hydrogen content of the molten metal, but far more often it appears to be an indication of the amount of hydrogen which that particular type of steel can hold under those chilling conditions and in an atmosphere of evolved hydrogen.

Drawing general conclusions from these results, it would appear that under the conditions in which the pencil tests were taken, a plain carbon steel can retain about 0.0003% of hydrogen. The effect of chromium in the steel raises the amount of hydrogen which can be held in the solid up to 0.0009%, and it is for this reason that the results have been tabulated in order of increasing chromium contents of the steels examined. Nickel up to 4% in steel does not appear to increase the amount of hydrogen retained in the solid pencil tests as compared with plain carbon steels. This may not necessarily mean that the solubility of hydrogen in nickel steel is no greater than it is in plain carbon steel, as the solubility and also the rate of diffusion of hydrogen might be greater.

It must be remembered, when considering the small quantities of hydrogen evolved from many of the samples collected by the balloon-tube method, that the apparatus was deliberately designed so as to be able to check the evolution of hydrogen, so that as much as possible would be retained in the solid sample for estimation in the usual manner by vacuum fusion. It was hoped that by some such means, coupled with rapid subsequent vacuum fusion, the evolved gas might be negligible, so that the solid sample retained substantially all of the hydrogen present in the molten steel. The authors' results show that for many of the molten steel samples examined they have not been able to suppress the evolution of hydrogen, and the significance of this fact is that such molten steel

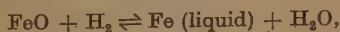
when solidifying in ingot form could have a considerable pressure of gaseous hydrogen in and/or around it. This does not mean that such ingots would be unsound in the solid state; on the contrary, it is known that from such molten metal sound ingots were produced.

There are several alternative hypotheses which could be made as to the factors which may have determined the hydrogen found in the authors' liquid steel samples, such as :

(1) That the hydrogen found in the liquid steel is merely that which has been added in the various raw materials, and which has not had the opportunity of escaping before the sample was taken. This implies that the slag was a material relatively impervious to the diffusion of hydrogen, and that the loss of hydrogen from the liquid metal was insufficiently rapid to take place while removing the metal from the furnace and the slag from its upper surface.

(2) That there is an equilibrium between the hydrogen in the liquid metal and slag, as was suggested by Kobayashi¹ for open-hearth furnaces and substantiated by Herasymenko and Dombrowski (*loc. cit.*) for both open-hearth and arc furnaces. This would mean that the authors' figures were dependent primarily upon the state of oxidation of the bath as well as the hydrogen content of the slag. Confirmation of this idea would involve the simultaneous determination of the hydrogen content of the slag, and this the authors did not do.

(3) That there is an equilibrium between the water vapour in the atmosphere and the hydrogen in the molten steel. The arcs might facilitate the interchange in an arc furnace. Otherwise interaction could occur during sampling when the bare metal surface was exposed to the atmosphere, and could similarly take place on the bulk of the metal during tapping and teeming. In connection with this hypothesis, if calculations, based on Chipman and Samarin's² work on the iron-oxygen-hydrogen system and Sieverts'³ solubility determinations for hydrogen in liquid steel, are made for the hydrogen content of molten steel in equilibrium with the amounts of water vapour normally present in the atmosphere, then the result is of the same order as what the authors find by direct determination. Thus, taking Sieverts' value for the solubility of hydrogen in molten iron at 1600° C., 0.0026%, and Chipman and Samarin's value of 0.88 for the reaction constant of :



the amount of hydrogen dissolved in the molten metal, $[\text{H}]$,

¹ Kobayashi, *Tetsu to Hagane*, 1938, vol. 24, p. 227.

² Chipman and Samarin, *American Institute of Mining and Metallurgical Engineers*, 1937, *Technical Publication No. 784*.

³ Sieverts, Zapf and Moritz, *Zeitschrift für physikalische Chemie*, 1938, A., vol. 183, p. 19.

and in equilibrium with a definite pressure of water vapour ($P_{\text{H}_2\text{O}}$ expressed in atmospheres) would be :

$$[\text{H}] = 0.0026 \sqrt{\frac{P_{\text{H}_2\text{O}}}{0.88 \times [\text{FeO}]}} \text{ at } 1600^\circ \text{ C.,}$$

from which it can be calculated that for an average value of water vapour of 8 mm. of mercury (equivalent to a relative humidity of 60% at 15° C.) and for an [FeO] content of 0.045%, which is equivalent to 0.010% of oxygen, the hydrogen dissolved in the molten metal at 1600° C. and in equilibrium with the water vapour would be 0.0013%. In the correspondence on an earlier publication of one of the present authors,¹ a somewhat similar deduction was drawn by Dr. N. P. Allen, only this was in connection with the authors' figures for the hydrogen contents of solid steel samples.

Whilst it is pointed out that the above calculated value for the equilibrium hydrogen content of molten steel is in agreement with the upper limit of what is actually found, it is not implied that the hydrogen found in steel necessarily (though it may be so) originates from atmospheric water vapour. One is accustomed to think of hydrogen being easily driven off from steel at high temperatures, and this calculation shows the limit to which hydrogen will be lost if the molten metal is in equilibrium with atmospheric water vapour. Moreover, Herasymenko and Dombrowsky's determinations of hydrogen and water in slag suggest that the presence of slag between the metal and the atmosphere might not seriously impede the attainment of such an equilibrium.

Apart from the significance of the actual results obtained, one important fact does emerge from the authors' investigations on the hydrogen content of liquid steel, and that is that the hydrogen found in cold steel samples need bear no relationship to what was present in the molten metal before casting. For steel-melting investigations it is clearly insufficient merely to determine the hydrogen content of the solid metal after casting.

The authors wish to thank the Directors of Messrs. Thomas Firth and John Brown, Ltd., and of Messrs. Firth-Vickers Stainless Steels, Ltd., for their agreement to the publication of the data given in this paper, the experienced steel-melters who have co-operated so well, and Mr. J. E. Wells, Assoc.Met., for valuable assistance.

¹ Newell, *Journal of The Iron and Steel Institute*, 1940, No. I., p. 243 P.

Section V.—General Summary.

Although the contributions to this Report are each preceded by a synopsis and contain an individual summary and conclusions, it will perhaps be useful to present a general summary referring to the most important aspects of these individual papers and to state the general position of this work as it now stands.

With the exception of the Section dealing with the sampling of liquid steel, no new principles have been introduced, and the Report deals essentially with improvements and refinements in the methods already dealt with by the Sub-Committee.

In Part A(a) of Section II. Mr. Sloman discusses the vacuum fusion method, which still remains the accepted standard method for the determination of total oxygen in iron and steel. Sources of error which have been observed during investigations on alloy steels and ferro-alloys are mentioned and are associated particularly with the presence of volatile metallic constituents. Mr. Sloman's contribution also contains an account of a series of experiments on a 13% manganese steel, undertaken to study the effect of the manganese-film formation on the oxygen value. Sub-section (b) of Part A contains a note by Dr. Swinden, Mr. Stevenson and Mr. Speight describing further experience with the fractional modification of the vacuum fusion method, and the results of an interesting application of the principle to a study of weld metal deposits are included.

Vacuum fusion and the fractional modification may be regarded as direct methods for the determination of oxygen; the residue methods, *i.e.*, the iodine and chlorine extractions, in which iron is chemically separated from a residue of non-metallic inclusions, the analysis of which leads to a calculated oxygen value, may be considered to be indirect methods. The aluminium reduction method, which, as Mr. Gray and Mr. Sanders state in sub-section (c) of Part A, continues to be used with success, occupies a somewhat intermediate position between the direct and indirect methods, the oxygen being obtained from alumina by chemical analysis of the sample after alloying with aluminium. This relatively inexpensive and rapid method is operated either in a hydrogen atmosphere or under reduced pressure, and has given results in very close agreement with those of vacuum fusion.

Turning now to the indirect or residue methods, which are described in sub-sections (d), (e) and (f) of Part A, admirable progress has been made in extending the applicability and increasing our knowledge of the significance of these methods. In sub-section (d), Mr. Colbeck and Mr. Craven describe experiments on the effect of increased chlorination temperatures on the composition of the residue obtained in the normal chlorination at 350° C. Increased chlorination temperature is necessitated by the presence in steel of

alloying elements, particularly large amounts of chromium. Reference is made to the earlier work of Wasmuht on this aspect of the chlorine method. Although the present experiments by Mr. Colbeck and Mr. Craven must be regarded as exploratory, they indicate that, with well-killed steels containing inclusions of a balanced character, an increase of chlorination temperature up to 500° C., at which chromium chloride is appreciably removed, effects little alteration in the quantity and composition of the non-metallic residue. Consequently, there is every hope that chromium steels will be examined satisfactorily by the chlorine method.

The fundamentals of the alcoholic iodine method have received further attention, and in sub-section (e) of Part A a critical summary of the three papers dealing with various aspects of the method is presented. Mr. Rooney describes in paper (e1) experiments on the effect of the water content of the methanol solvent and shows that the presence of water causes an increase in the content of iron oxide found in the separated residue. Control of the purity of the methanol supplies as received by using sensitive hydrometers is suggested by Mr. Rooney as a means of avoiding unnecessary purification of the methanol by distillation over calcium. In paper (e2) Mr. Speight discusses the behaviour of carbon and phosphorus in the alcoholic iodine method and their effect on the composition of the separated residue. A suggested explanation based on adsorption is put forward in connection with the contamination of the residue by oxides of these two elements. The possibility of a similar effect in the case of other constituents of the residue is also indicated, and the need for subsequent treatment of the residue to remove the excess contamination is stressed. Initial experiments using a solution of ammonium tartrate for this purpose have given a qualified success. As indicated in the Third Report of the Oxygen Subcommittee, it is not unusual for an accepted method to be modified to suit different types of material. Consequently, it must be recognised that decomposition of steel by alcoholic iodine does not necessarily separate only the oxygen-bearing non-metallic inclusions. For a correct measure of the oxygen content any contaminants present should be identified and their effect on the determination assessed. A similar conclusion is reached by Mr. Rooney, who, in paper (e3) of this sub-section, describes the interference due to the presence of aluminium in steel. From three steels containing rather more aluminium than is normally present in carbon steels, alcoholic iodine residues with excessive contents of alumina were obtained. The alumina was separated by an after-treatment into an insoluble fraction, which presumably occurs as alumina in the steel, and a soluble portion, comprising other aluminium compounds separated during the alcoholic iodine extraction. By these experiments, our knowledge of the limitations and uses of the alcoholic iodine method has been definitely advanced.

The aqueous iodine method, on which Mr. Westwood reports

progress with its application to pig and cast iron in sub-section (f), continues to be used substantially as described in the Third Report of the Oxygen Sub-Committee. The possible effect of the surface film (which has been shown to be a maximum on millings) has been recognised and the method has been modified to allow the use of a solid sample, thereby reducing this effect considerably.

The position, therefore, with regard to methods of analysis for oxygen in iron and steel may be summarised as follows :

In the vacuum fusion method we have a thoroughly reliable method of determining the total oxygen in steel and steelmaking alloys. A suitable technique must be employed when the sample has a high content of certain volatile constituents, such as manganese, but the necessary precautions are well established.

The aluminium-reduction method has been extensively examined on a variety of commercial steels and again, with suitable control, has been found to be uniformly satisfactory for the determination of total oxygen.

It will, however, be readily understood that the determination of total oxygen provides information of only limited value, and therefore other methods have been investigated to assess the content of the respective oxides.

The alcoholic iodine method has been most exhaustively studied and its value and limitations are now reasonably well understood. By this method results comparable with those obtained by the vacuum fusion process can readily be obtained on plain carbon and low-alloy steels, which, after all, constitute a very large proportion of our steel production. Favourable results have been obtained on some commercial nickel-chromium alloy steels, but stable carbides are a source of interference with the method. Low-carbon rimming steels containing a high proportion of ferrous and manganous oxides do not always furnish satisfactory results.

The chlorine extraction method gives promise of more successful application to a wider variety of steels, particularly those containing carbide-forming elements, *e.g.*, chromium, but there appear to be limitations to the method, such as are demonstrated in the low results obtained for rimming steel.

The modification of the vacuum fusion process whereby the extraction is carried out in fractional stages has been shown to produce results in good agreement with those of the orthodox vacuum fusion method as regards total oxygen, and some interesting results are obtained by this method in separating the oxygen into its constituent oxides. Further work still requires to be done, however, before the process can be claimed to have been established as universally reliable for all combinations of oxides.

Finally, the aqueous iodine method has been used, with interesting results, by the British Cast Iron Research Association on pig iron, although the Sub-Committee prefer to express no opinion as to its reliability when dealing with steel samples.

In Section II., Part B, sub-section (a), methods for the determination of hydrogen in ferrous materials are discussed by Dr. Newell. Almost all these methods involve vacuum extraction of the hydrogen at high temperatures, either above or below the melting point of the alloy. Hence, not only is hydrogen determined by the vacuum fusion process, but also by the vacuum-heating method at temperatures of the order of 600° C. and the latter technique has been used by several Members of the Sub-Committee. Following the usual custom of the Oxygen Sub-Committee, new apparatus are described in detail so as to assist other workers who may be called upon to install similar equipment. Accordingly, full particulars of equipment now in use at the United Steel Companies and I.C.I. (Alkali) Laboratories, together with further developments in the Brown-Firth Research Laboratories apparatus, are given by Mr. Stevenson and Mr. Speight, by Mr. Colbeck and Mr. Craven and by Dr. Newell in sub-sections (b2), (b3) and (b1), respectively.

It is believed that the subject matter of Section II., Part C, in which Dr. Swinden first reviews methods of analysis for nitrogen in steel will be particularly valuable in view of the wide interest in this element and its effects (sub-section (a)). Two methods are most commonly adopted for the determination of nitrogen, namely, the vacuum fusion and the chemical distillation procedures (sub-sections (b) and (c)). The accuracy of the vacuum fusion technique for nitrogen has been noted by earlier workers and the subsequent work of the Sub-Committee has, in the main, confirmed this conclusion. Reference to certain difficulties is made, but, provided that suitable precautions are taken, accurate results are obtained. The Sub-Committee have devoted considerable attention to a study of the chemical distillation method as applied to carbon and alloy steels and their detailed recommendations are given in sub-section (c), which concludes with a few notes on possible developments in chemical methods. The chief difficulty in the chemical method appears to be in obtaining complete decomposition of the nitrogen compounds and subsequent conversion to ammonia. The recommended procedure includes the established distillation over caustic soda, and detailed comments on the blank troubles attendant on this method are made.

In Section III. accounts are given of some of the uses to which the afore-mentioned methods of analysis have been put during the examination of ferrous materials and for the purposes of fundamental investigation. Since much of this work has required the use of a ferrous base material of very low oxygen content, it is perhaps apposite that a description of the preparation of this oxygen-free iron, known as N.P.L. iron, Mark 2, should appear in a Sub-Committee Report. Part (a) of Section III., by Mr. Sloman and Mr. Cook, gives an account of this iron base, and the thanks of the Sub-Committee are due to the National Physical Laboratory for their painstaking efforts in the preparation and supply of the N.P.L. iron, Mark

2, which has advanced materially the progress of the Sub-Committee's investigations.

Further research on the surface oxygen film on iron and steel is described by Mr. Sloman and Mr. Rooney in Part (b) of Section III. The present contribution is an excellent and concise statement, containing much data of paramount importance to a sound understanding of surface films on metals. The extent of interference, attributed to the surface film, according to the type of sample used in the usual methods for the determination of gases, is carefully stated. The use of milled samples in any oxygen determination is not to be recommended.

The reaction of rimming steels to the residue methods was noted in the Third Report of the Sub-Committee, and a further study of several types of rimming steel is submitted by Mr. Rooney and Dr. Jones in Part (c) of Section III. It was shown by Dr. Swinden and Mr. Stevenson in the Third Report (p. 384 P) that solution in alcoholic iodine at 65° C. gave low oxygen results, owing presumably to attack of the solvent on the basic oxides of iron and manganese contained in the low-carbon rimming steel examined. Mr. Rooney and his collaborator have studied in greater detail the application of the alcoholic iodine method to rimming steels, and the earlier conclusions are substantially confirmed. It must be emphasised that the difficulty is most acute with rimming steels of low carbon content and consequent high oxygen, occurring mainly as iron and manganese oxides. With such steels, Mr. Rooney has modified the standard procedure and investigated the effect of a heat treatment of the sample, and, whilst a certain measure of improvement is achieved, further difficulties in the non-decomposition of sulphide and carbide have been encountered. X-ray examination was useful in detecting the presence of manganese sulphide and iron carbide, but did not detect any oxide, although a vacuum fusion determination on a residue revealed the presence of 0.009% of oxygen (*see Appendix*).

Section III.(d), by Dr. Hatfield and Dr. Newell, describes typical results for the gas contents of the raw materials used in steelmaking processes. Considerable variations in the gas contents are recorded, and their significance is discussed. A diminution of the hydrogen content is achieved by heating ferro-alloys, &c., at 650–850° C., but this procedure is often accompanied by increased oxidation.

The information derived from the co-operative examination of the oxygen of typical acid and basic slags by the usual methods of determination and reported by Mr. Stevenson and Mr. Speight in Section III.(e) is most valuable. This investigation shows that our present methods of examination satisfactorily account for the oxygen content of acid silicates, but that with basic inclusions recovery may be incomplete. Although it may indeed be stated that such inclusions do not occur normally in steel, knowledge of the limitations of the present methods for oxygen is advanced substantially by these experiments.

A concise paper jointly by Mr. Gray, Mr. Sanders, Mr. Graham and Mr. Short in Section III.(f) describes the occurrence of elemental silicon in residues from the aluminium reduction method when applied to high-silicon iron and the means adopted to overcome this peculiar interference. In addition to being of considerable scientific interest, this unexpected behaviour of silicon is typical of the small but troublesome features which arise all too frequently when new methods are applied to unusual materials.

Mr. Pearce, in Section III.(g), states the position with regard to the oxide inclusions in pig and cast irons, reviewing the evidence presented by microscopic and chemical means.

In Section III.(h), the results obtained collaboratively for oxygen, hydrogen and nitrogen in a series of commercial alloy steels are shown and amplified by suitable comments by Dr. Swinden. Since these results serve to illustrate many of the observations made in this present Section, further comment is unnecessary.

The foregoing relates to the examination of cold samples, and it is felt that the work which the Sub-Committee set out to do in the establishment of methods has, speaking generally, been completed. It is quite clear, however, that it would be of far greater value to be able to determine the gas content (particularly oxygen and hydrogen) during the process of steel manufacture. It is on this subject that the Sub-Committee will concentrate their efforts in the future. Attention is therefore directed to Section IV., which, it is submitted, lays the basis for future work on the determination respectively of oxygen and hydrogen in liquid steel. The importance is elaborated by Dr. Swinden in the Introduction, and in Section IV.(a) he and Mr. Stevenson give an account of their experience in furnace-stage oxygen determination, dealing particularly with the bomb method of sampling, the method of dealing with the sample and some typical results obtained. In Section IV.(b) Dr. Hatfield and Dr. Newell deal with the sampling of liquid steel for its hydrogen content. Two new methods, the notched chill-mould method and the balloon-tube method, are described and a series of interesting results are reported. The conclusion is drawn that the hydrogen content of small cast steel samples need bear no relationship to that originally present in the molten steel.

Those Members of the Sub-Committee engaged in industrial laboratories are pleased to record their acknowledgment of the facilities provided by their respective Companies and the permission of their Directors for the publication of the various papers.

The best appreciation which the co-operating Members of the Sub-Committee can have is a full and frank discussion on this Report, in which it is hoped that there may be expressions of the value of this work from an industrial point of view and suggestions which the Sub-Committee can consider for incorporation in their future programme.

CORRESPONDENCE.

Dr. U. R. EVANS (Cambridge University) wrote: In their valuable paper on "The Surface (Oxygen) Film on Iron and Steel and its Effect on the Determination of Oxygen" (Section III. (b)) Mr. Sloman and Mr. Rooney state that the surface oxygen on iron (sawn discs)—as estimated by vacuum fusion—is 4.0×10^{-6} g. per sq. cm. It would be interesting to compare this with estimates made by other methods, but this requires a knowledge of the period of exposure to air. Since freshly abraded iron takes up oxygen very rapidly, it would be satisfactory if further particulars could be given of the time of exposure, and of the temperatures prevailing during the making of "cuts."

Nevertheless, some comparison with the electrometric results of Miley and the present writer¹ is possible. The oxidation curves obtained at Cambridge showed that freshly abraded iron takes up oxygen very rapidly for the first 5 min. at 18° C. in dry air, but that after about 20 min. the oxidation has become slow. The points fall well on the curves, and the accuracy of the method has been checked against weight-loss measurements made *on the same specimens*. The oxidation rate depends on the surface condition, but the mean thickness (as ferric oxide) reached after 130 min. at 18° C. (when the growth rate was of the order of 0.1 Å. per min.) varied between 180 Å and 210 Å. This is equivalent to about 10×10^{-6} g. per sq. cm. of Fe_2O_3 , whereas the authors' figure of 4×10^{-6} g. per cm. of oxygen, if present as ferric oxide, would represent 13×10^{-6} g. per sq. cm. of Fe_2O_3 .

The authors state that Vernon, Wormwell and Nurse,² using "the original method of Evans," based on aqueous iodine solution, obtained films contaminated with hydroxide. In the original paper³ it is stated that the contamination—the existence of which was fully recognised—can in many cases be removed in 2 min. by dilute hydrochloric acid, in which the oxide flakes themselves remain almost unchanged after many hours. Clearly, however, the method is unsuited for measuring film thickness, and has never been used for such purposes at Cambridge. The anodic stripping method—conducted in hydrogen—has been used to a small extent for estimations of thicknesses,⁴ but in most cases microgravimetric or electrometric methods have been preferred in the Cambridge Laboratory. Wherever possible, methods have been checked

¹ H. A. Miley and U. R. Evans, *Journal of the Chemical Society*, 1937, p. 1295.

² W. H. J. Vernon, F. Wormwell and T. J. Nurse, *Journal of the Chemical Society*, 1939, p. 621.

³ U. R. Evans, *Journal of the Chemical Society*, 1927, p. 1025.

⁴ U. R. Evans and J. Stockdale, *Journal of the Chemical Society*, 1929, p. 2656.

against one another; in the case of films of iodide¹ and sulphide,² it has been possible to obtain *three* estimates of the film thickness upon *each* specimen by three *independent* methods, the agreement being, in most cases, satisfactory.

Attention may also be drawn to the optical method of Winterbottom,³ and the vacuum microbalance technique of Gulbransen.⁴

Each of the methods mentioned above has its drawbacks, but they are essentially designed to measure superficial—as opposed to internal—oxide, and thus merit consideration.

The alcoholic iodine method developed in the two Teddington Laboratories is a very great improvement on the aqueous iodine method, which is unlikely to be used for film studies again. Nevertheless, used intelligently in a manner designed to minimise contamination, the aqueous iodine method is capable of giving valuable information; there is no reason to think that any of the main conclusions based on the researches carried out at Cambridge with the method in 1927 are wrong. It is the writer's view that stripping in an aqueous solution without contamination does not represent an impossibility, but the iodine solution is not suitable for this purpose.

Dr. L. REEVE (Appleby-Frodingham Steel Co., Ltd., Scunthorpe, Lincs.) wrote: The paper by Dr. Swinden and Mr. Stevenson on "The Determination of Oxygen in Liquid Steel" (Section IV. (a)) is, I believe, the first one published by The Iron and Steel Institute on this aspect of oxygen determination in steel and as such will be welcomed by all who have direct contact with practical steel-making.

Although our investigations have not been published we have carried out several tests at Appleby-Frodingham on the original Herty spoon method of oxygen determination in liquid steel. As indicated on p. 399 P of the authors' paper, the results were erratic and the work was discontinued.

During the last two years, and simultaneously with the investigations reported in the authors' paper, we have re-examined the Herty spoon method, using an improved technique, and have recently compared these results with the bomb sampling method. We have been able to obtain consistent results with each method considered separately (consistency being judged by close agreement of two samples taken immediately one after the other), but the bomb method has invariably given lower oxygen figures, confirming that extraneous oxidation takes place in the spoon samples. A summary

¹ U. R. Evans and L. C. Bannister, *Proceedings of the Royal Society*, 1929, A., vol. 125, p. 380.

² L. E. Price and G. J. Thomas, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 332.

³ A. B. Winterbottom, *Nature*, 1937, vol. 140, p. 364.

⁴ E. A. Gulbransen, *Transactions of the Electrochemical Society*, 1942, vol. 81, p. 327.

of our recent results is shown in Fig. A, in which oxygen values are plotted against carbon in the sample, using both methods. Tests were taken in all cases in the final stages of heats in our large Appleby tilting furnaces, shortly before tapping.

On the same diagram is plotted the theoretical carbon-oxygen equilibrium curve calculated from data by Fethers and Chipman,¹ corrected to 1600° C. and a pressure of 1.5 atm. It will be noted that the spoon-killed samples gave results averaging at least 0.015% of oxygen higher than the bomb samples. There is an appreciable scatter of results, as one would expect in view of the number of variables likely to affect the oxygen content, but there is no doubt of the general trend.

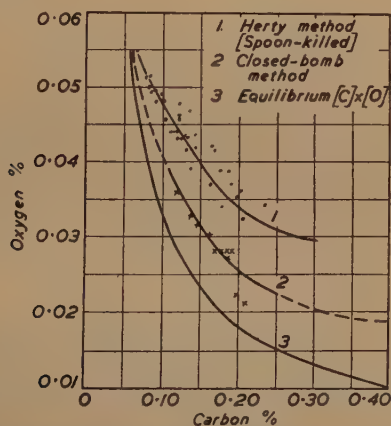


FIG. A.—Relationship between Oxygen and Carbon in the Open-Hearth Bath.

The relationship between oxygen and iron in the slag was very much less clearly defined, also that between oxygen and residual manganese. This is in agreement with the results of Washburn and Philbrook.² The authors do not discuss this aspect of their results, but it is clear from the figures in Table LXX. that on the whole their results lie nearer curve 3 than curve 2. There are several exceptions, however, some oxygen values being even below curve 3, whilst the last three determinations are nearer curve 2. These divergencies are, no doubt, associated with the stage of the heats at which the samples were taken. More information on this aspect of the problem would be of interest.

¹ *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1940, vol. 140, p. 170. See discussion by Fethers on paper by Marshall and Chipman, *Transactions of the American Society for Metals*, 1942, vol. 30, Sept., p. 743.

² *American Institute of Mining and Metallurgical Engineers, Proceedings of the Open-Hearth Conference*, 1940, p. 187. See also the 1938 Conference.

Turning now to the practical details of taking the bomb samples, reference is made in the paper to the fact that a technique was required at Appleby-Frodingham, different from that described by the authors. Without going into too great detail, the main difference was essentially in the dimensions of the bomb. We found it necessary to reduce the wall thickness of the bomb slightly and to increase the diameter of the neck appreciably. Otherwise we were liable to run into trouble with slag freezing to the cap, partial filling of the bomb and similar difficulties. With our bomb (which is made of steel) immersion times of 12-15 sec. in slag and steel gave us satisfactory results.

Some trouble must be expected by those beginning to use this new technique until the conditions have been standardised.

The heterogeneity of the bomb samples in our case was of the order reported by the authors, similar results for oxygen content being obtained at any point in the bomb below the pipe.

Mr. C. S. GRAHAM (Messrs. John Lysaght, Ltd., Scunthorpe) wrote: I should like to ask whether the vacuum fusion method is suitable for free-cutting steels containing, say, 0.25% of sulphur. Hitherto I have seen no mention of the effect of high sulphur on the final results.

SUB-COMMITTEE'S REPLY.

On behalf of the Oxygen Sub-Committee the following replies have been prepared by the authors of the papers discussed.

Mr. SLOMAN and Mr. ROONEY, the authors of the paper on "The Surface (Oxygen) Film on Iron and Steel and its Effect on the Determination of Oxygen" (Section III.(b)), replied: We wish to thank Dr. Evans for his very interesting contribution to the discussion. We are, of course, fully aware of the very valuable work which has been carried out at Cambridge and elsewhere, to which Dr. Evans gives references, but would point out that, as the Oxygen Sub-Committee are concerned with methods for the determination of the internal oxygen in iron and steel, the work described in the present paper was undertaken solely with a view to ascertaining what errors, if any, were introduced into the results obtained by the various methods, owing to the surface oxygen normally and unavoidably present on specimens of different types—solid cylinders, discs, millings, &c. We were not concerned with the more fundamental aspects of surface oxidation nor with the respective merits of the various methods which have been put forward for estimating or stripping the surface film, except insofar as the results obtained had a bearing on the work of the Sub-Committee. It was for this reason that the work of Vernon and his collaborators was discussed

at somewhat greater length than that of other investigators, since they and we had examined the same materials under exactly similar conditions of preparation.

In preparing the specimens to which Dr. Evans refers, the conditions employed were those which might be expected to approximate closely to those which would be used in preparing similar specimens for one or other of the methods for determining internal oxygen being investigated by the Sub-Committee. For example, the sawn discs of pure iron were prepared as described in the paper on a lathe in a workshop of normal temperature and humidity—the comparison specimens (solid cylinders) being machined at the same time. Each specimen took about 15 min. to prepare and was then immediately transferred without handling to a desiccator, where it would remain while the rest of the specimens were being produced—a total period of perhaps 2 hr. The specimens would then be exposed to the atmosphere again for a few minutes for weighing before being introduced into the vacuum fusion apparatus, which would then be immediately evacuated.

The agreement which Dr. Evans deduces between the present results and those obtained by Riley and himself by the electrometric method is perhaps not quite so good as he has suggested, since he compares an electrometric result of 10×10^{-6} g. per sq. cm. of Fe_2O_3 obtained on *abraded* iron with a vacuum fusion result of 13×10^{-6} g. per sq. cm. of Fe_2O_3 obtained on *sawn* discs of iron. In order to make the comparison quite strict it would have been preferable to take the vacuum fusion result for *abraded* iron given in Table XXXII., which is equivalent to 5×10^{-6} g. per sq. cm. of Fe_2O_3 .

Dr. SWINDEN and Mr. STEVENSON, the authors of the paper on "The Determination of Oxygen in Liquid Steel" (Section IV.(a)), replied: We thank Dr. Reeve for his interesting contribution and would like, at the same time, to express our appreciation of the collaboration that has always been forthcoming in the melting shops of the Appleby-Frodingham Steel Company.

The additional data requested are contained in Table A, which sets out the stage in the heat at which the various samples referred to in Table LXX. were taken. It will be noted, as indeed was pointed out by Dr. Reeve, that these samples were taken at various stages during the manufacture of the steel and do not necessarily represent equilibrium conditions.

Dr. SWINDEN, replying to Mr. Graham, wrote: A large number of vacuum fusion determinations has been carried out at Stocksbridge on high-sulphur steels, including sections from the ingot examined by Dr. Gregory¹ and Mr. Whiteley. The sulphur content of this ingot was of the order of 0.45%. No evidence of sulphur interference has been noted, and, so far as we are aware, there is

¹ *Journal of The Iron and Steel Institute*, 1941, No. II., p. 9 p.

TABLE A.—*Further Data regarding Furnace Condition of Bomb Samples. (See Table LXX.).*

Cast No.	Sample.	Clock Time.	Furnace Conditions.	Carbon. %.	Oxygen Vacuum Fusion. %.
34/2238	1	12-20	Clear melted. 10 min. after lime and spar.	0-44	0-007 ₄
	2	13-45	Towards end of refining.	0-13	0-024 ₂
	3	14-16	Tapping. After spiegel and ferro-manganese.	0-14	0-026 ₃
30/4600	1	13-45	Clear melted. 15 min. after lime and spar.	0-65	0-013 ₄
	2	16-30	Tapping. After ferro-manganese.	0-22	0-016 ₇
31/501	1	11-00	Towards end of refining.	0-15	0-018 ₄
	2	11-15	Tapping. After spiegel and ferro-manganese.	0-17	0-017 ₇
31/508	1	11-05	Clear melted. 45 min. after lime and spar.	0-33	0-008 ₄
	2	11-43	Towards end of refining.	0-19	0-016 ₆
	3	11-50	Tapping. After spiegel and ferro-manganese.	0-19	0-018 ₁
35/7148	1	10-20	Clear melted. 20 min. after lime.	0-42	0-007 ₂
	2	11-00	Towards end of refining.	0-26	0-012 ₄
35/7156	...	14-30	Clear melted. 30 min. after lime and spar.	0-29	0-012 ₁
31/599	...	10-20	Clear melted. 30 min. after lime and spar.	0-48	0-006
31/572	1	12-00	Clear melted. 35 min. after lime and spar.	0-23	0-012 ₂
	2	13-10	Towards end of refining.	0-15	0-025 ₄
30/4591	1	10-15	Clear melted. 45 min. after lime and spar.	0-80	0-004 ₄
	2	12-50	Towards end of refining.	0-24	0-021 ₇
	3	13-10	Tapping. After spiegel and ferro-manganese.	0-27	0-017 ₁
36/5453	...	15-25	10 min. before tapping. Before spiegel and ferro-manganese.	0-20	0-031 ₄
27/5679	...	10-40	Tapping. Before ferro-manganese.	0-12	0-034 ₄
35/6847	...	11-47	5 min. before tapping. Before ferro-manganese.	0-12	0-037

no decomposition of sulphides under the conditions of the vacuum fusion method. High-sulphur steels do not evolve more than the same mere trace of gas, absorbed by sodium hydroxide solution, as is found with normal low-sulphur steels.

The Fourth Report of the Oxygen Sub-Committee was also presented for discussion at a Joint Meeting of the Sheffield Metallurgical Association, the Sheffield Society of Engineers and Metallurgists and The Iron and Steel Institute, held in the Assembly Room, Royal Victoria Station Hotel, Sheffield, on December 4th, 1943, at 2.30 P.M., under the chairmanship of Professor J. H. Andrew (Past President of the Sheffield Society of Engineers and Metallurgists, Member of Council of The Iron and Steel Institute). The discussion will be recorded in the No. I. volume of the *Journal of The Iron and Steel Institute* for 1944.

THE STRUCTURE AND SEGREGATION OF TWO INGOTS OF INGOT IRON, ONE CONTAINING LEAD.¹

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(Figs. 4 to 13 = Plates XXIII. to XXVIII.)

SUMMARY.

The object of this investigation was to determine the segregation in a low-carbon steel ingot containing lead as compared with a similar ingot free from lead. For this purpose two ingots were obtained from the same melt, a lead addition being made to the mould in one case but not the other. The axial faces of the ingots were prepared for macro-examination, sulphur- and lead-printing, and samples were obtained for chemical analysis, micro-examination and radiographic examination.

It was found that, apart from noticeable lead segregation at the extreme base of the ingot, the distribution of lead was very similar to that of the other elements examined. Machinability tests on sections cut from the cast ingot confirmed that the energy absorbed in machining the lead-bearing steel was 25% less than with the lead-free steel.

Introduction.

A CONSIDERABLE quantity of lead-bearing steel is now being used for purposes where ready machinability is required. Some information upon the mode of segregation of the lead in lead-bearing steel ingots is already available. For example, Guillet² has given figures for lead segregation in steel ingots of 0.2% and 0.35% carbon content and Nead, Sims and Harder³ have shown figures comparing lead segregation in killed and unkilld steels.

As information was required upon the segregation in ingots of very low carbon content two steel ingots of ingot-iron quality, one of them containing lead, were selected for comparative examination, the results of which are reported here. The two ingots were cast from the same melt, a lead addition being made to the mould in one case but not in the other. The ingots were obtained from Messrs. Guest Keen Baldwins Iron and Steel Co. Ltd., and the casting particulars have been made available through the courtesy of Mr. Norman Gray. The structure, segregation and properties of the two ingots are described below.

¹ A communication from the Armament Research Department, formerly the Research Department, Woolwich, received April 8, 1943.

² *Revue de Métallurgie, Mémoires*, 1940, vol. 37, p. 29.

³ *Metals and Alloys*, 1939, vol. 10, pp. 68, 109.

Casting Conditions.

The charge, consisting of one-third hot iron and the remainder scrap, weighed 75 tons. The additions were 4 tons 7 cwt. of scale, a total of 8 tons 10 cwt. of limestone and 45 lb. of aluminium. The ingots were teemed in pairs through two fireclay ladle nozzles of $1\frac{1}{2}$ in. dia. Forty-three ingots each of $32\frac{1}{2}$ cwt. and two of 45 cwt. were cast. These last two formed the fifth pair and were the ones selected for the investigation, one of them being a plain ingot iron and the other a leaded ingot iron. Fifty-three pounds of fine lead shot were added to the stream from the ladle into the mould, commencing when a pool of metal about 4 in. deep had collected. The dimensions of the moulds were as follows :

Overall height	6 ft. $2\frac{1}{2}$ in.
Internal dimensions :	
Top section	$18\frac{1}{8}$ in. square.
Bottom section	$16\frac{1}{8}$ in. square.
Wall thickness at bottom	$4\frac{1}{2}$ in.

The time of charging the furnace was $5\frac{3}{4}$ hr., and melting down took 6 hr. The total time taken from the commencement of charging to tapping was $14\frac{1}{2}$ hr. The analysis of the pit sample was carbon 0.02%, manganese 0.037%, sulphur 0.039% and phosphorus 0.01%.

*Ingot Examination.**Macrostructure.*

The ingots were sectioned longitudinally and the axial faces ground and polished. Sulphur prints were obtained from both the ingots and lead prints from the lead-bearing ingot. In order to develop the macrostructure fully, use was made of three separate etching reagents, namely, dilute nitric acid, acid ammonium persulphate and Stead's reagent. Different structures were obtained with each of these reagents and are reproduced together with the sulphur prints in Figs. 4 to 11. For convenience the photographs were obtained with the solutions on the ingot sections and in the case of the copper reagent etch a thin film of copper covered the steel.

Comparing the results obtained with the different etching reagents, Stead's copper reagent was the only one adequately showing the primary structure, and the columnar nature of the outside rim of the ingot is quite clearly indicated. The nitric-acid etch gives a much cleaner appearance to the section and clearly reveals the final crystal structure; at the same time the blow-holes appear dark. The ammonium-persulphate reagent shows a greater degree of contrast between the outside pure region and the inner impure core; this reagent was the only one which at the same time developed the strain markings left by the original grinding operation adopted in the preparation of the surface.

From a study of these photographs it would appear that :

(a) The rim is composed of wholly columnar primary crystals.

(b) The rim columnar crystals in these rimming ingots are very much coarser than those normally found in killed steel.

(c) Although the crystal structure of the rim is fairly well defined, there is practically no evidence of primary crystals in the core of the ingot, only a few faint patches of segregates being observed.

(d) The blow-holes on the inside of the rim are at the tips of the columnar crystals.

(e) The purer rim extends not quite to the main line of blow-holes about 2 in. in from the edge.

(f) The lower third of the rim in the lead-bearing ingot contains a number of intercrystalline blow-holes, which considerably reduce the effective thickness of this portion of the rim.

Only in the case of the nitric-acid etching was the appearance of the ingot axial faces influenced by the presence of lead. The lead-bearing ingot, *TTP*, had a bright uniform surface almost devoid of crystal structure, whereas the lead-free ingot, *TTQ*, showed the crystals very clearly and the core etched much darker than the rim. Although these ingots are of high purity, the difference in composition across the rim crystals was sufficiently great for this difference to be shown up on etching with the copper reagent, so that the rim crystals are easily discernible.

Chemical Analysis.

Samples for chemical analysis were obtained from the twelve positions shown in Fig. 1, using a $\frac{3}{4}$ -in. dia. drill for a depth of 1 in. The twelve positions included those standardised by the Committee on the Heterogeneity of Steel Ingots to show heterogeneity. The results of the analyses are shown in Table I.

From top to bottom of the ingot the lead content decreases in the core, but increases in the rim. Apart from the higher lead content in the rim at the bottom of the ingot, the segregation of lead closely follows that of the segregating elements sulphur and phosphorus, in spite of the different modes in which these three elements occur in steel and in the manner of addition of the lead. The carbon, silicon and manganese contents are so very low that segregation of these elements is virtually absent. The noticeable copper content of the ingots will be observed.

Further data were obtained by sampling from a 1-in. wide slice cut across the middle of the ingot, ten samples being obtained from the edge to the centre-line. Samples were milled from across the slice over areas $\frac{1}{8}$ in. wide by $\frac{1}{4}$ in. deep, the purpose of these analyses being to determine the distribution in the direction of growth of the ingot. Only ten positions in each bar were selected, so that the

TABLE I.—*Chemical Analysis.*

Position.	Leaded Ingot Iron Ingot TTP.							Ingot Iron Ingot TTQ.							Ingot Com- mittee's Standard Position.
	C. %.	Si. %.	S. %.	P. %.	Mn. %.	Pb. %.	Cu. %.	C. %.	Si. %.	S. %.	P. %.	Mn. %.	Cu. %.		
1	0.02	<0.01	0.090	0.019	0.04	0.36	0.12	0.02	0.01	0.067	0.017	0.05	0.13	H	
2	0.02	<0.01	0.072	0.016	0.035	0.32	0.13	0.02	0.01	0.058	0.015	0.04	0.13	D	
3	0.02	<0.01	0.052	0.013	0.045	0.30	0.12	0.02	0.01	0.048	0.014	0.04	0.12	C	
4	0.02	<0.01	0.049	0.013	0.05	0.26	0.12	0.02	0.01	0.032	0.011	0.04	0.11	B	
5	0.02	<0.01	0.080	0.017	0.05	0.34	0.13	0.02	0.01	0.064	0.016	0.05	
6	0.02	<0.01	0.053	0.014	0.04	0.29	...	0.02	0.01	0.051	0.014	0.04	
7	0.02	<0.01	0.073	0.016	0.04	0.31	...	0.03	0.01	0.060	0.015	0.03	0.12	G	
8	0.03	<0.01	0.054	0.015	0.05	0.22	0.11	0.05	0.01	0.037	0.014	0.04	0.12	F	
9	0.02	<0.01	0.039	0.009	0.04	0.22	0.10	0.02	0.01	0.018	0.007	0.04	
10	0.02	<0.01	0.043	0.009	0.04	0.24	...	0.02	0.01	0.024	0.009	0.05	
11	0.04	<0.01	0.045	0.012	0.04	0.32	...	0.02	0.01	0.024	0.008	0.04	0.10	A	
12	0.03	<0.01	0.042	0.011	0.04	{0.71 0.53 } 0.63 0.66 }	0.10	0.02	0.01	0.026	0.011	0.05	

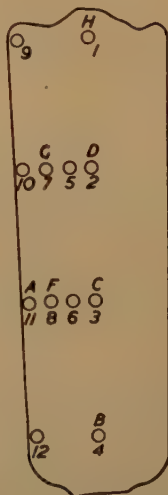


FIG. 1.—Positions from which Samples for Chemical Analysis were taken.

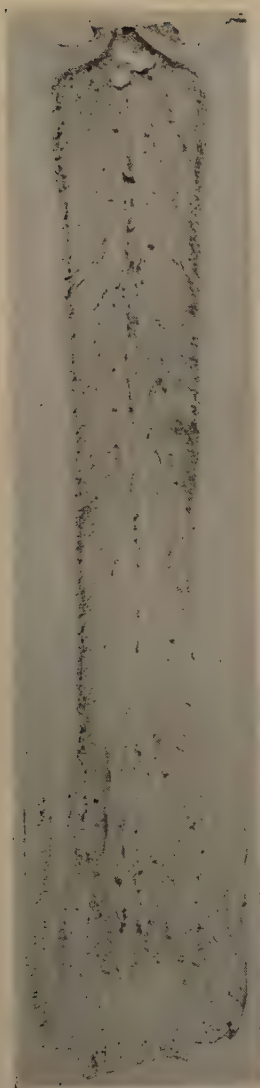


FIG. 4.—Sulphur Print.



FIG. 5.—Ammonium-Persulphate Etch.

FIGS. 4 and 5 (*see* Figs. 6 and 7).—Lead-Bearing Ingot-Iron Ingot *TTP*. $\times \frac{1}{14}$.

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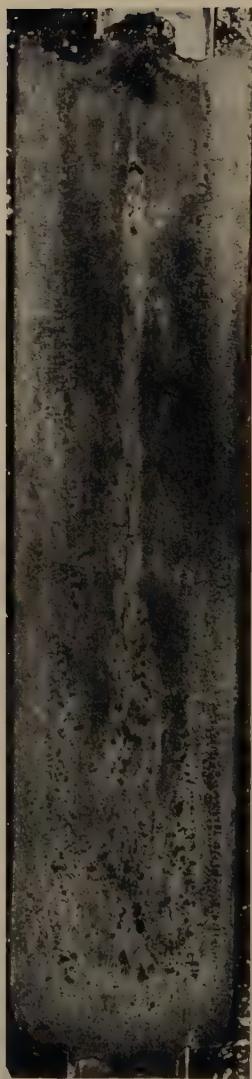


FIG. 6.—Nitric-Acid Etch,
FIGS. 6 and 7 (see Figs. 4 and 5).—Lead-Bearing Ingot-Iron Ingot *TTP*. $\times \frac{1}{4}$.

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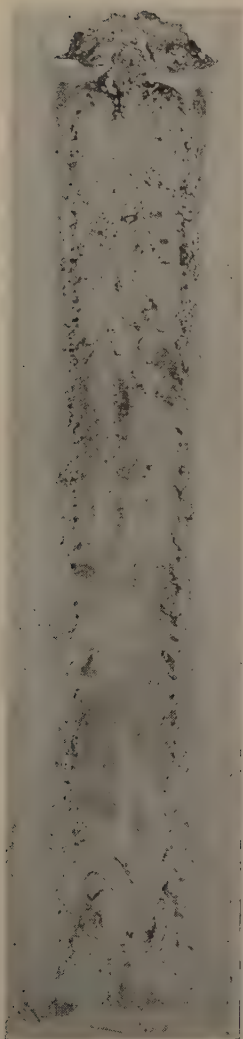


FIG. 8.—Sulphur Print.



FIG. 9.—Ammonium-Persulphate Etch.

FIGS. 8 and 9 (see Figs. 10 and 11).—Lead-Free Ingot-Iron Ingot *TTQ*. $\times \frac{1}{11}$.



FIG. 10.—Nitric-Acid Etch.



FIG. 11.—Copper-Reagent Etch.

FIGS. 10 and 11 (see Figs. 8 and 9).—Lead-Free Ingot-Iron Ingot *TTQ*. $\times \frac{1}{14}$.

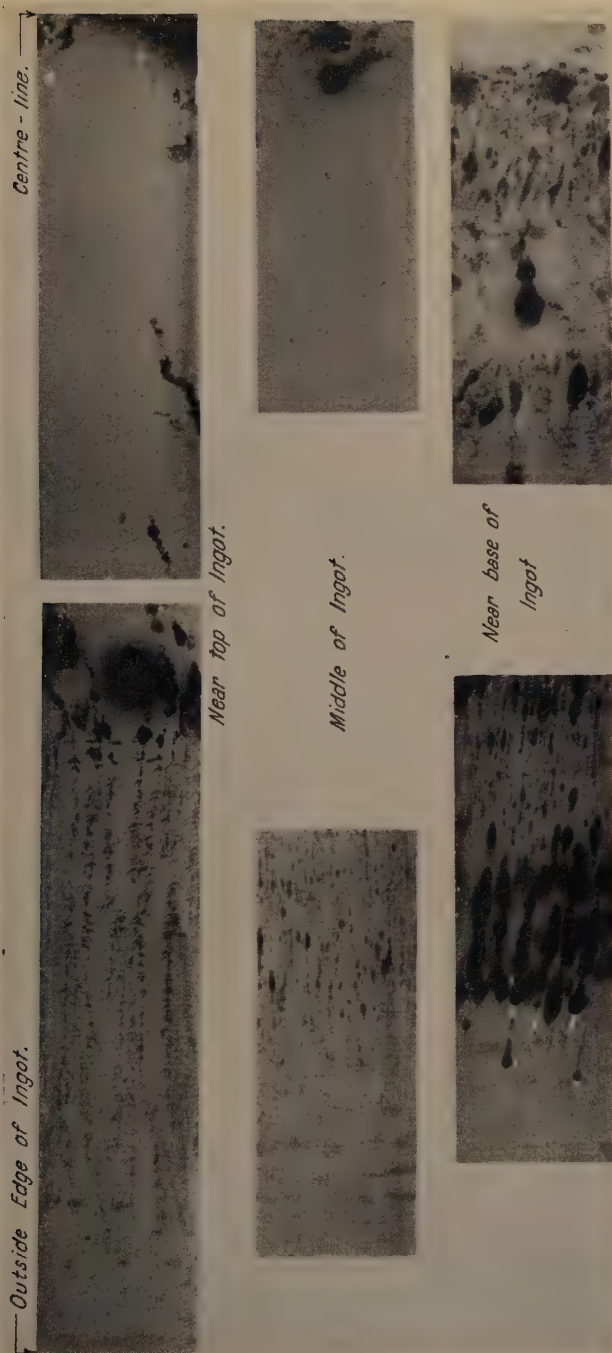


FIG. 12.—Lead-Bearing Ingot TTP. Radiographs of axial slices, 0.25 in. thick.

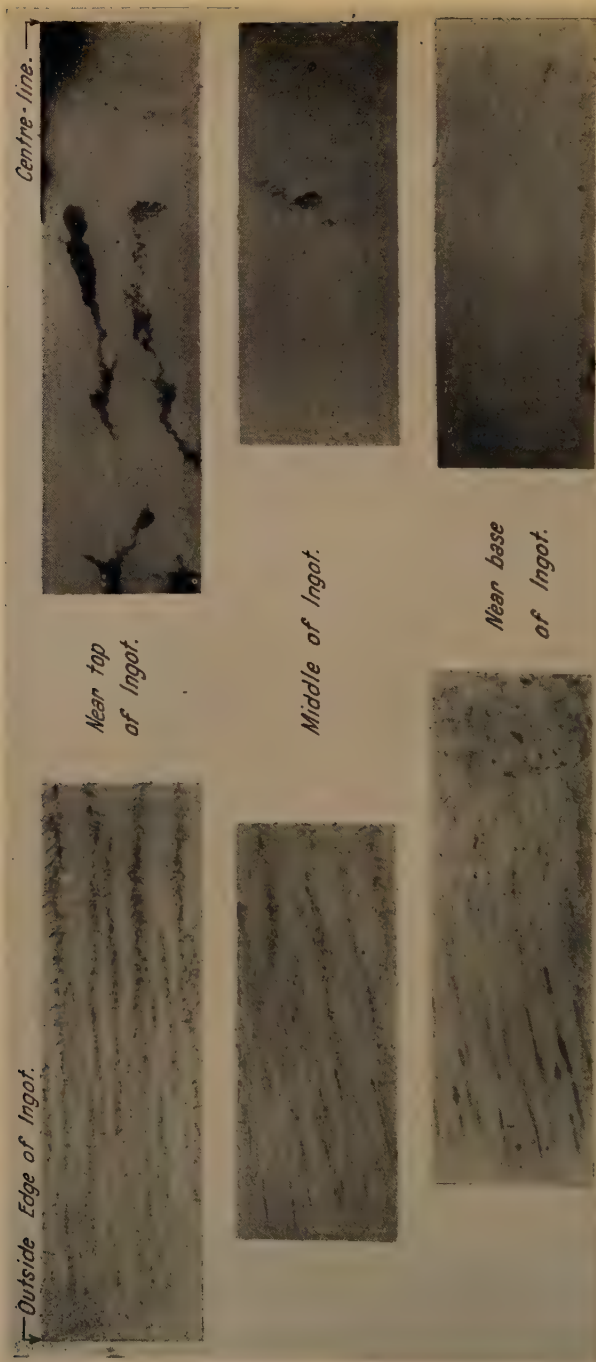


FIG. 13.—Lead-Free Ingot T7Q. Radiographs of axial slices, 0.25 in. thick.

sampling was much less complete than that carried out, for example, by Swinden.¹ The results are given in Table II. and are plotted in Figs. 2 and 3. The determinations for carbon and sulphur in this

TABLE II.—Composition from Edge to Centre at Middle of Ingot.

Position.	Leaded Ingot TTP.				Lead-Free Ingot TTQ.		
	C. %.	S. %.	P. %.	Pb. %.	C. %.	S. %.	P. %.
Outside edge 1 .	0.05	0.041	0.014	0.33	0.045	0.034	0.016
2 .	0.04	0.034	0.010	0.29	0.048	0.026	0.013
3 .	0.04	0.020	0.009	0.21	0.034	0.019	0.014
4 .	0.03	0.025	0.011	0.29	0.020	0.029	0.019
5 .	0.04	0.039	0.013	0.36	0.032	0.054	0.021
6 .	0.053	0.075	0.018	...	0.06	0.108	0.023
7 .	0.035	0.066	0.017	0.30	...	0.072	0.027 [#]
8 .	0.026	0.063	0.013	0.30	0.033	0.053	0.021
9 .	0.032	0.045	0.016	0.31	0.023	0.053	0.023
Centre of ingot 10 .	0.051	0.043	0.013	0.24	0.025	0.074	0.019

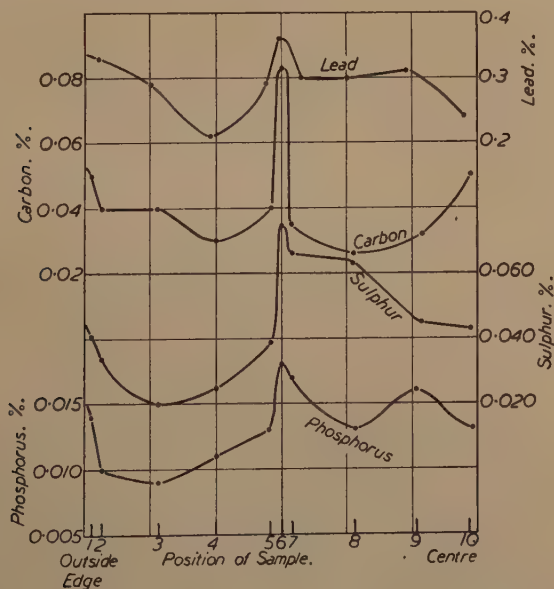


FIG. 2.—Lead-Bearing Ingot TTP. Composition from edge to centre. E

series were made by micro-chemical analysis, and it is probable that the values obtained are of higher accuracy than those given in Table I.

The general form of the curves is similar to that normally found

¹ Seventh Report on the Heterogeneity of Steel Ingots, p. 15, *Iron and Steel Institute*, 1937, *Special Report No. 16*; Eighth Report, p. 17, *Iron and Steel Institute*, 1939, *Special Report No. 25*.

in rimming steels, although the peak at the position corresponding with the commencement of the core is possibly more pronounced than usual, especially with respect to sulphur and carbon. The distribution of lead across the ingot follows the same general rule as for the other constituents examined, in spite of the different mode of occurrence of this element.

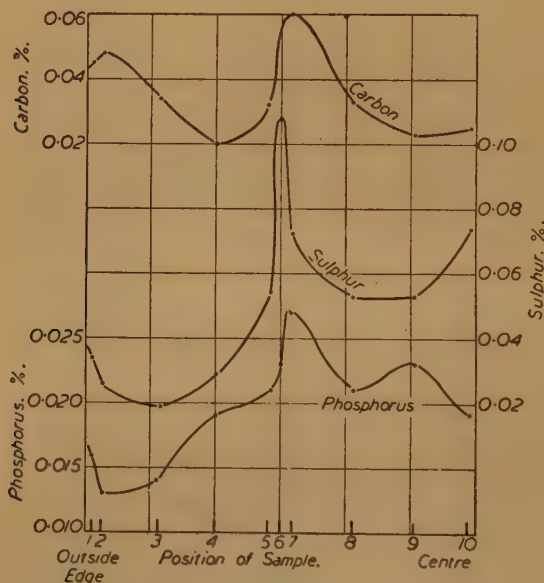


FIG. 3.—Lead-Free Ingot TTQ. Composition from edge to centre.

One interesting feature brought out by the carbon analyses is that the carbon content at the extreme edge of the ingot was appreciably higher than that found in the core; as this feature occurs in both the leaded and the lead-free ingot, it is clearly not due to experimental error. A study has been made of the segregation in the steel ingots as reported by the Ingots Committee and three examples Nos. 62,¹ 64² and 65² are of similar or only slightly higher carbon content. Of these examples No. 62 shows a similar effect of a lower carbon content at the core than at the outside of the rim, the carbon at the A, F and C positions being respectively 0.039%, 0.033% and 0.021%. Example 64 shows a different form of segregation; here the carbon contents are respectively 0.05%, 0.07% and 0.08% at

¹ Fifth Report on the Heterogeneity of Steel Ingots, p. 32, *Iron and Steel Institute*, 1933, *Special Report No. 4*.

² Sixth Report on the Heterogeneity of Steel Ingots, pp. 19, 23, *Iron and Steel Institute*, 1935, *Special Report No. 9*.

the *A*, *F* and *C* positions, whereas in example 65 the values are respectively 0.04%, 0.04% and 0.05%. It does appear, therefore, that where the carbon content is really low the percentage of carbon at the extreme outside edge of the ingot may be appreciably higher than that in the core. On the other hand, it is also probable that sampling from three positions *A*, *F* and *C* hardly gives an adequate picture of the segregation from edge to centre of an ingot, and it is advisable that a number of samples be taken at increasing distances from the edge in order to obtain a true impression of the segregation of the elements. The results obtained with the present ingots show that the segregation found in example 62, which had hitherto been looked upon as an exceptional case, may indeed be quite representative of ingots of very low carbon content.

The present results tend to confirm the hypothesis of Hultgren and Phragmén that for liquid steel of lower carbon content than the balanced composition, which they put at around 0.06% of carbon, the carbon would decrease in the liquid metal during freezing under gas evolution. This aspect has been recently discussed by Binnie,¹ who estimated that with a manganese-free steel at atmospheric pressure the balanced composition would be 0.045% of carbon, increasing to 0.063% under a pressure of 2 atm.

In view of the differences in the values obtainable in the samples subjected to microchemical analysis as given in Table II. and those determined by normal methods as given in Table I., it is probable that where conclusions on segregation are to be drawn from analysis figures for elements present in very small quantities the methods adopted for analysis should be sufficiently sensitive to determine quite small changes in composition, and care is necessary in taking the sample for analysis and in selecting positions in the ingot from which the analytical samples are obtained.

Microstructure.

Samples for micro-examination were obtained from the slices cut from the different positions selected for the tests on machinability. In view of the known difficulty with selective etching treatments for lead a comparison was made of the structures of the lead-bearing and lead-free steels. The structures were generally similar to those usually found in rimming steels, as already described, for example, by Swinden.² Numerous small inclusions of the sulphide type were observed in the core of the ingot, whereas in the rim the inclusions were for the most part too small to be identifiable.

No evidence was obtained of indisputable lead deposits in samples from the cast ingot. The only difference observed under the microscope was a greater tendency for the leaded ingot to show cavities formerly occupied by inclusions.

¹ *Journal of The Iron and Steel Institute*, 1942, No. II., p. 283p.

² Ninth Report on the Heterogeneity of Steel Ingots, p. 17, *Iron and Steel Institute*, 1939, *Special Report No. 27*.

Samples which were hot-rolled contained short streaky particles in longitudinal sections of the leaded ingot but not in the lead-free ingot; after annealing at 950° C. no difference could be observed in the leaded and lead-free sections, indicating a break-up or spheroidising of the supposedly lead streaks in the leaded ingot.

Lead-Printing.

Lead prints were obtained from axial faces of the leaded ingot after sulphur-printing. The method used was a modification of that developed by Ledloy, Ltd., and is described in the Appendix.

Tests were subsequently made on axial sections 6 in. deep cut across the whole width from the lead-free as well as from the lead-bearing ingot. There was pronounced segregation at the extreme base of the leaded ingot, where quite large globules of lead had collected, although the addition of lead had been made some time after the commencement of pouring.

The leaded-steel prints showed a darker background, particularly in the core, but spotting due to lead was not readily discernible; the lead-free ingot gave a colourless print.

Machinability.

As the purpose of lead additions is to improve machinability, tests were made of sections cut from six positions representing the core and rim at upper, middle and lower positions in each ingot. The upper position was about 9 in. from the extreme top of the ingot and the lower position about 1 ft. from the bottom. It is appreciated that the requirements for high machining speeds are usually confined to material in the forged and rolled condition and not in the condition as cast. The Oxford Airey machine used for the determination of relative machinability has been previously described.¹

TABLE III.—*Relative Machinability.*

Position in Ingot.	Energy Absorbed. Ft.lb. per cu. in.		Percentage Reduction in Energy Absorbed in Machining. $\frac{TTQ - TTP}{TTQ} \times 100.$
	Lead-Bearing Steel <i>TTP.</i>	Lead-Free Steel <i>TTQ.</i>	
Upper rim . . .	$\times 10^4$ 2.61	$\times 10^4$ 3.37	23.5
Upper core . . .	2.45	2.83	13.4
Middle rim . . .	2.45	3.74	34.5
Middle core . . .	2.25	3.06	26.5
Lower rim . . .	2.38	3.64	34.5
Lower core . . .	2.51	2.83	11.3
Mean . . .	2.44	3.24	24.7

The figures given in Table III. show the energy absorbed in removing one cubic inch of metal with a tool having an action

¹ Kenneford, *Journal of the Institute of Metals*, 1939, vol. 65, p. 79.

similar to that of a milling cutter. The conditions of cutting were : Tool, high-speed steel; top rake, 20° ; cooling agent, sulphonated oil solution; feed, 0.02 in.; depth, 0.02 in.

These figures clearly show that the energy absorbed in machining tests on the lead-bearing steel averaged 25% less than that with the lead-free steel. Furthermore, in both ingots more energy was required in the machining of the outer rim than of the less pure core, the average figures being 3.58 and 2.91 ft.lb. per cu. in. for the rim and core of *TTQ* and 2.48 and 2.40 ft.lb. per cu. in. for the lead-bearing ingot *TTP*; in the latter steel a high lead content at the lower rim resulted in a lower energy figure at this position and so modified the average for the *TTP* series, but the presence of lead obviously had a notable effect in improving the machinability of the rim in ingot *TTP*.

Mechanical Properties.

Sections cut from the upper rim of each of the two ingots were hot-rolled to 0.3 in. and then annealed at 950° C. The mechanical properties obtained on the two materials were identical :

	Yield Point,* Tons per sq. in.	Max. Stress. Tons per sq. in.	Elonga- tion. %	Reduction of Area, %	Vickers Diamond Hardness.
Lead-containing ingot iron .	8.4	18.2	48	78	84
Lead-free ingot iron .	8.3	18.4	43	77	85

* By dividers.

X-Ray Examination.

With a view to detecting fine porosity and the presence of segregates of lead, an X-ray examination was carried out upon slices 1 in. wide and 0.25 in. thick cut from the centre to the edge of the ingot; samples were obtained from the top, middle and base of the ingot. For comparison purposes samples from the lead-free ingot *TTQ* were also examined. In order to determine the degree of local porosity a control sample was prepared by hot-rolling the slab cut from the rim of the lead-bearing ingot and machining this to the dimensions of the slices under examination, except that the thickness varied in ten steps from 0.25 in. to 0.025 in.; this control sample was radiographed alongside the cast sections. Representative radiographs are reproduced in Figs. 12 and 13. From a study of the X-ray negatives it appeared that :

(a) No evidence of lead was to be observed in sections cut from the rim of the ingots, except near the base where occasional large deposits were found associated with blow-holes.

(b) Several small globules of lead occurred in the core, more especially in the upper half of the ingot, particularly at the commencement of the core and also down the centre of the ingot.

(c) Correlation between the radiographs and the lead contents at different positions in the ingot suggests that X-ray examination, although valuable as showing the degree of lead dispersion,

does not permit an estimate to be formed of the quantity of lead present.

(d) The core of the ingot appeared to be sound away from the large cavities, but the rim, which on visual examination gave the impression of being sound, was characterised by fine interdendritic columnar porosity. This porosity in the rim was also shown up by deep-etching polished sections, but it is thought that the radiographs illustrate the extent of the porosity much better than would etching. A comparison of radiographs of the rim with the radiograph of the forged and stepped bar showed that the interdendritic porosity may amount locally to as much as 10-20%.

Conclusions.

A comparative examination was carried out of the structure, segregation and machinability of two ingot-iron ingots prepared from the same melt, one of them containing lead.

The segregation of the lead, as determined by chemical analysis, lead-printing and macro-examination, was generally similar to that observed for sulphur and phosphorus, but, in addition, coarse deposits of lead were found at the extreme base of the ingot. The coarser nature of the particles of lead in the core of the lead-bearing ingot was confirmed by radiographs, which showed isolated small particles of lead in ingot sections cut from the core, whereas no clear evidence of lead was obtained in sections cut from the rim.

The macrostructure was developed by etching with various reagents, but it was only in the case of the nitric-acid etch that any influence due to the lead addition was observed; the lead-bearing ingot showed less evidence of crystal structure or segregation in the core.

The primary structure as developed by a copper reagent showed that the rim was composed of coarse crystals, but the "coring" of the primary crystals in the middle, less pure, portion of the ingot was insufficient for the etching reagents employed to develop the primary crystal structure of this part of the ingot.

Machinability tests on sections cut from different portions of the two ingots confirmed that with the lead-bearing one the energy absorbed was about 25% less than with the lead-free steel. In both ingots the rim absorbed more energy during machining than did the core, and the beneficial effect of the lead was more pronounced at the rim.

Acknowledgments.

Thanks are due to Dr. W. A. Wood, who carried out the radiological examination, to Mr. P. G. Ward and Miss I. H. Hadfield for the chemical analyses and to Mr. A. S. Kenneford for the machinability tests.

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APPENDIX.—*Lead-Printing.*

This method was developed by Ledloy, Ltd. The following three solutions are used :

Printing Solution A.

25 g. of tartaric acid.
100 g. of ammonium acetate.
250 ml. of water.
The solution was saturated with H_2S .

Developing Solution B.

A saturated solution of H_2S in water.

Clearing Solution C.

10% aqueous ammonium persulphate or tartaric acid solution saturated with H_2S .

Lead prints were taken of slabs cut from the two ingots. The surface was prepared as follows : The metal was polished smooth down to No. 1 emery cloth, then cleaned and degreased. The surface was etched with 50% nitric acid; the surface should be etched as evenly as possible. The acid was then washed off and the surface quickly dried. The gelatined paper soaked in solution *A* was at once applied and pressed well and evenly into contact, using a rubber roller, the back of the paper being kept moist with solution *A*. After 2–3 min. the paper was stripped off and developed in solution *B*. At this stage iron, dissolved off with the lead, caused intense black staining, much of which washed off into the solution. This staining was removed by washing in solution *C*; as this caused some fading of the lead-printing it was necessary after clearing in solution *C* to wash the print in clean solution *B*. The print was next washed in water and dried quickly, using methylated spirits, since moist lead sulphide tends to oxidise, thus obscuring the print.

Prints were taken of sections of the lead-free ingot as well as of the lead-bearing one, and the following conclusions were reached : Satisfactory results are not obtainable by taking two lead prints consecutively from the same surface, unless the latter is machined after taking the first print, since the prints so obtained are poor and inconclusive. In any case the whole process is sensitive to dirt, and staining is common, considerable skill being required to obtain consistently good prints. However, it seems that most of the colorations obtained are due to lead; this is confirmed by the lack of marking on prints of *TTQ2*, and by the respective distribution of colour in the various sections of *TTP* examined. By photographing the final prints greater contrast may be obtained. False conclusions may be avoided to a great extent by taking several prints of the same specimen and considering the results so obtained in conjunction with each other.

If the specimen is not machined after each print is taken, not only does the general background become fainter but also fine porosity leads to brown spot staining, which was found to arise from rust in the cavities.

Additionally, the presence of copper was found to lead to some staining around cavities when the specimen was not re-prepared.

[This paper was discussed jointly with the following one by T. Swinden on "Leaded Manganese-Molybdenum Steel."]



LEADED MANGANESE-MOLYBDENUM STEEL.¹

By T. SWINDEN, D.MET. (CENTRAL RESEARCH DEPARTMENT, THE UNITED STEEL COMPANIES, LTD., STOCKSBRIDGE, NEAR SHEFFIELD).

(Fig. 11 — Plate XXIX.)

Paper No. 13/1943 of the Alloy Steels Research Committee.

SYNOPSIS.

Tests were carried out on material from a non-leaded and a leaded ingot of manganese-molybdenum steel in order to determine the effect of lead (0.19%) on the mechanical properties, including the machinability. The leaded steel had a slightly coarser inherent grain size and less depth-hardenability than the non-leaded steel.

The properties measured in the tensile test at room temperature were similar for the two steels in the form of flat and round bars. The notched-bar impact toughness of the leaded steel at room temperature was rather less than that of the non-leaded steel.

At elevated temperatures the maximum-stress values of both steels were similar, but the ductility, as measured by elongation and reduction of area, was lower in the case of the leaded steel, particularly in the transverse direction. The Izod impact values of the leaded steel also were lower at elevated temperatures.

The Barr-Bardgett creep-stress values of the two steels at 500° C. were identical, whilst no significant difference was shown by the figures for damping capacity.

When treated to a tensile strength of 65 tons per sq. in. the fatigue ratio and notch sensitivity (rotary bending) of the two steels were similar. When treated to the lower tensile strength of about 55 tons per sq. in. the non-leaded steel had a higher fatigue ratio (rotating cantilever) and slightly greater notch sensitivity than the leaded steel. The fatigue ratio (direct stress) of the non-leaded steel compared with the leaded steel was slightly higher when treated to 65 tons per sq. in. and slightly lower when treated to about 55 tons per sq. in.

The machinability of the leaded steel was markedly superior to that of the non-leaded steel.

A COMPREHENSIVE study has been made of material from two ingots of manganese-molybdenum steel, to one of which lead was added, giving a content of 0.19% in the steel. The purpose of the tests was to obtain comparable data for the leaded and non-leaded steels.

Acid Open-Hearth Steel Cast W2722.

Cast Analysis.

Carbon	0.36%	Phosphorus	0.045%
Manganese	1.43%	Molybdenum	0.43%
Silicon	0.225%	Nickel	0.16%
Sulphur	0.032%	Chromium	0.11%

¹ Received September 2, 1942. This paper is published by authority of the Alloy Steels Research Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

The ingots were cast uphill with brick tops; they measured 19 in. at the top, tapering to 17 in. at the bottom, and weighed 45 cwt. They were rolled by normal procedure into $4\frac{1}{4}$ -in. by $2\frac{7}{8}$ -in. slabs, from which were subsequently rolled $4\frac{1}{2}$ -in. by $\frac{5}{8}$ -in. bars and 1-in., $\frac{3}{4}$ -in. and $\frac{7}{8}$ -in. dia. bars.

Lead Exudation Tests.

These tests were carried out on the slabs from which the test material was obtained and showed that the slabs were free from lead segregation.

McQuaid-Ehn Grain Size.

The McQuaid-Ehn grain sizes of the two steels were as follows :

Leaded	Grades 4 to 6, mainly 5 to 6.
Non-leaded	Grades 6 to 7, mainly 6.

The leaded steel was slightly coarser in grain size than the non-leaded steel.

Jominy End-Quench Hardenability Tests.

Standard Jominy end-quench hardenability tests were carried out on both steels. The results are shown graphically in Fig. 1.

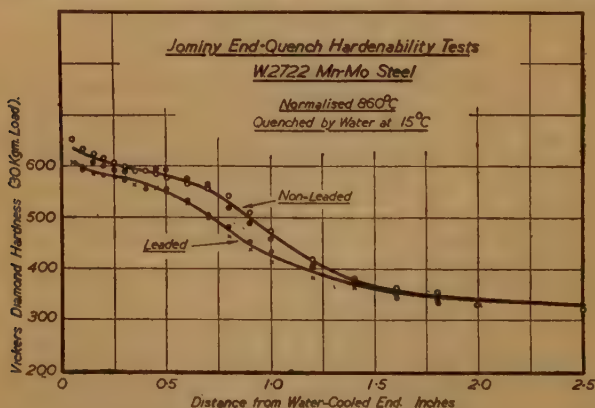


FIG. 1.

On the basis of these results the non-leaded steel shows greater hardenability, as regards both maximum hardness and depth of hardening, than the leaded steel.

TENSILE AND IMPACT TESTS AT ROOM TEMPERATURE.

(a) Tests on Flat Bars.

Tensile and impact tests were carried out at room temperature on longitudinal and transverse specimens oil-quenched and water-

quenched, respectively, from 840° C. and tempered at 640–650° C., the specimens being normalised at 910° C. for 2 hr. before final heat treatment. The results are given in Table I.

TABLE I.—*Flat Bars. Tensile and Impact Tests at Room Temperature.*

	Longitudinal.		Transverse.	
	O.Q.	W.Q.	O.Q.	W.Q.
<i>Non-Leaded.</i>				
Maximum stress. Tons per sq. in.	55.2	53.9	55.9	55.5
Yield point. Tons per sq. in.	52.2	51.0	53.5	52.9
Elongation on $4\sqrt{A}$. %	25.3	26.7	16.0	18.0
Reduction of area. %	64.5	64.5	35.5	39.7
Izod impact value:				
Ft. lb.	72, 85, 63	94, 69, 85	13, 13, 13	12, 13, 12
Average	73	82	13	12
<i>Leaded.</i>				
Maximum stress. Tons per sq. in.	53.8	55.2	56.1	55.0
Yield point. Tons per sq. in.	52.2	54.5	54.1	53.3
Elongation on $4\sqrt{A}$. %	25.3	24.0	16.6	17.3
Reduction of area. %	62.4	59.6	35.5	35.5
Izod impact value:				
Ft. lb.	74, 73, 73	65, 82, 58	11, 10, 10	11, 10, 11
Average	73	68	10	11

The difference in the effect on the tensile and impact properties of water-quenching compared with oil-quenching is negligible in both steels.

The tensile-test results show only comparatively slight differences for the leaded compared with the non-leaded steel in both the longitudinal and the transverse directions.

Both steels undergo a marked but normal reduction in elongation and reduction of area in the transverse compared with the longitudinal direction.

The impact figures of the non-leaded steel are, in general, slightly superior to those of the leaded steel in the two directions. The figures obtained on transverse specimens are low in both steels.

(b) *Tests on Round Bars.*

Lengths of 1-in. diameter bar for tensile and impact tests were heat-treated to give 53, 58 and 65 tons per sq. in. tensile strength, the tests including determinations of the limit of proportionality and Young's modulus of each specimen. The results are given in Table II., and stress-strain curves for the various tests are shown in Fig. 2.

The maximum-stress and limit-of-proportionality figures for the

TABLE II.—*Round Bars. Tensile and Impact Tests at Room Temperature.*

Steel :	Non-Leaded.			Leaded.		
	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 650° C. 1 hr.	O.Q. 840° C., T. 620° C. 1 hr.	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 650° C. 1 hr.	O.Q. 840° C., T. 620° C. 1 hr.
Max. stress. Tons per sq. in. . .	54.1	56.8	66.4	54.2	56.8	65.6
Yield stress. Tons per sq. in. . .	52.0	52.0	64.0	49.8	52.4	63.0
Limit of propor- tionality. Tons per sq. in. . .	48.4	50.0	60.0	48.0	50.0	60.8
Elongation on 2 in. % . . .	25.0	26.0	21.5	22.0	24.0	21.0
Reduction of area. % . . .	63.6	63.6	57.2	61.6	61.6	57.2
Izod impact value :						
Ft. lb.	79, 88, 79	81, 84, 72	58, 52, 58	71, 59, 72	59, 65, 61	44, 44, 47
Average	82	79	56	67	62	45
Modulus of elasti- city. Tons per sq. in.	12,800	12,750	12,800	12,550	12,800	13,300

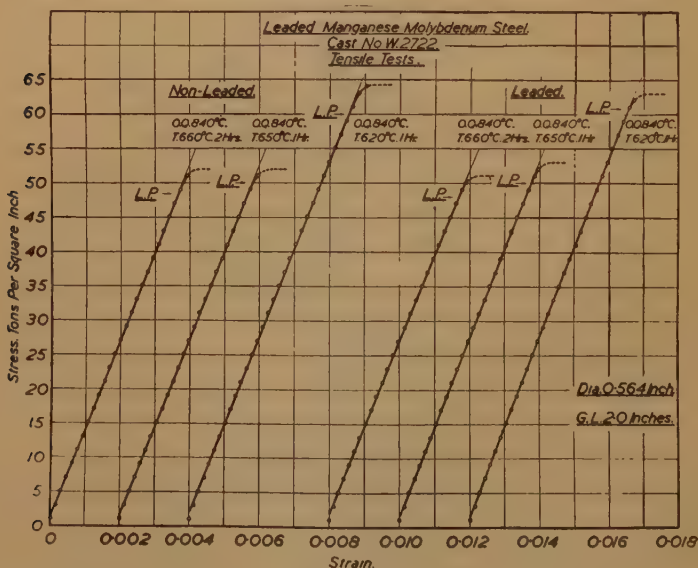


FIG. 2.

two steels treated to the three tensile strength values are respectively in very close agreement, whilst the yield-stress values differ only slightly, the general tendency being for those of the leaded steel to be lower than those of the non-leaded steel. There are only slight differences between the ductility figures of the two steels, as measured

by elongation and reduction of area, the general tendency being for the leaded steel to be slightly less ductile than the non-leaded steel. The leaded steel shows appreciably less ductility, as measured by the notched-bar impact test, than the non-leaded steel when the tensile strength is within the range 54–66 tons per sq. in.

The modulus-of-elasticity figures of the non-leaded steel are similar, irrespective of tensile strength, but those of the leaded steel show a definite progressive increase with increase in tensile strength from 54 to 66 tons per sq. in. When the tensile strength is of the order of 66 tons per sq. in. the modulus of elasticity of the leaded steel is appreciably greater than that of the non-leaded steel but similar when the tensile strength is 56·8 tons per sq. in.

TENSILE AND IMPACT TESTS AT ELEVATED TEMPERATURES.

(a) Tests on Flat Bars.

Tensile tests were carried out at temperatures of 300°, 350°, 400° and 450° C. on longitudinal and transverse specimens oil-quenched from 840° and tempered at 650° C., the specimens being normalised at 920° C. for 2 hr. before final heat treatment. In addition, impact tests on the leaded steel were carried out on longitudinal and transverse specimens similarly heat-treated, to cover the range of

TABLE III.—*Flat Bars. Tensile and Impact Tests at Elevated Temperatures.*

	Temp. of Test, ° C.	Non-Leaded.		Leaded.	
		Long.	Trans.	Long.	Trans.
Max. stress. Tons per sq. in.	300	58·1	57·5	57·9	57·2
	350	53·6	54·4	53·8	52·8
	400	50·1	49·6	50·2	49·4
	450	45·1	45·0	45·2	44·3
Elongation on $4\sqrt{A}$. %.	300	27·3	20·0	20·7	9·0
	350	26·0	22·0	17·3	8·7
	400	25·3	20·3	14·0	8·7
	450	26·7	21·3	19·3	11·3
Reduction of area. %.	300	53·2	31·9	31·9	12·6
	350	62·4	39·7	27·7	15·6
	400	62·4	46·8	24·1	10·6
	450	68·1	49·6	46·8	19·9
Izod impact values. Ft.lb.	250	56	15	47	10
	300	46	15	44	10
	350	42	15·5	42	10
	400	42	12·5	29	8
	450	30	10	25	8
	500	29	9·5	23	6
	550	25	8	23	7
	600	47	9	55	7

temperature from 250° to 550° C., with a further test at 600° C. on a longitudinal specimen.

A standard rate of straining of $\frac{1}{24}$ in. per min. was adopted in the tensile tests, the rate being increased to $\frac{1}{2}$ in. per min. after passing the maximum stress. The results are given in Table III., and the elongation, reduction-of-area and Izod impact values are shown graphically in Fig. 3.

FLAT BAR
LEADED AND NON-LEADED STEELS.

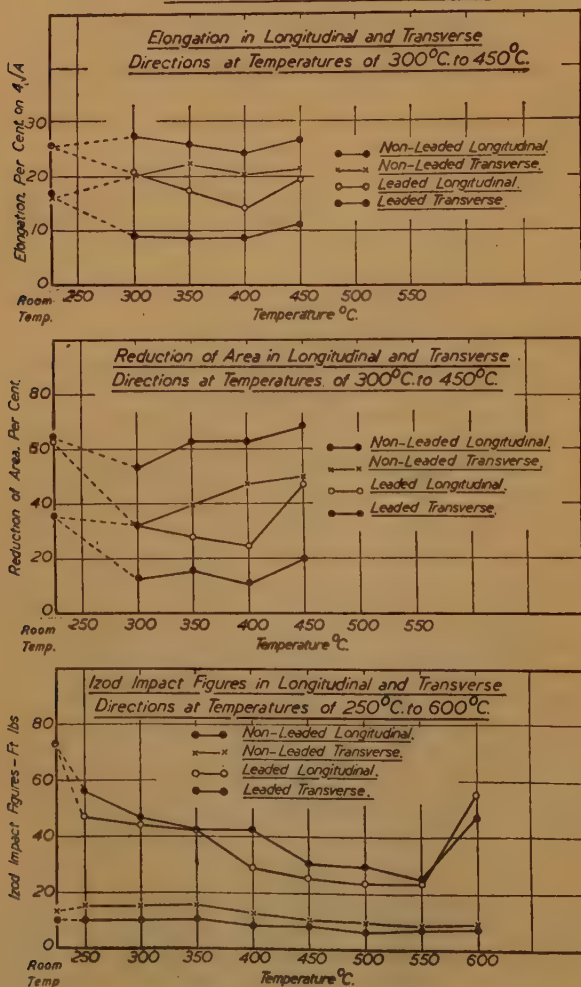


FIG. 3.

The maximum-stress figures of the longitudinal and transverse specimens of the non-leadcd and leadcd steels are respectively similar, and all show a gradual decrease as the test temperature rises from 300° to 450° C.

The elongation figures of the longitudinal and transverse specimens of both the non-leadcd and leadcd steels are at a minimum in the tests at 400° C. The values for the leadcd steel are appreciably lower than those of the non-leadcd steel, particularly in the transverse direction.

The reduction-of-area values of the longitudinal and transverse specimens of the non-leadcd steel increase as the temperature is increased from 300° to 450° C.; the leadcd steel, however, shows minimum values at 400° C. in the tests on specimens taken in both directions. The figures for the leadcd steel are markedly lower than those of the non-leadcd steel, particularly in the tests on transverse specimens and especially at 400° C.

TABLE IV.—Round Bars. Tensile and Impact Tests at Elevated Temperatures.

	Temp. of Test. ° C.	Non-Leaded.	Leaded.
Max. stress. Tons per sq. in.	250	57.6	57.8
	300	56.9	56.3
	350	52.3	53.7
	400	49.0	49.3
	450	43.2	44.3
	500	38.4	37.4
	550	32.1	34.1
Elongation on $4\sqrt{A}$. %.	250	24.0	20.0
	300	27.3	18.7
	350	28.7	16.0
	400	24.7	16.0
	450	25.7	22.0
	500	26.8	24.0
	550	28.0	24.7
Reduction of Area. %.	250	56.7	39.7
	300	56.7	31.9
	350	59.6	24.1
	400	62.4	27.7
	450	68.1	53.2
	500	73.0	64.5
	550	82.3	78.0
Izod impact values. Ft.lb.		Av'ge.	Av'ge.
	250	67, 62 64	52, 49 50
	300	66, 63 64	44, 40 42
	350	56, 53 54	41, 39 40
	400	48, 45 46	33, 34 33
	450	37, 32 34	26, 25 25
	500	26, 27 26	19, 21 20
	550	25, 28 26	18, 19 18

The results of Izod impact tests on the non-leaded and leaded steel in the longitudinal direction show decreasing values as the test

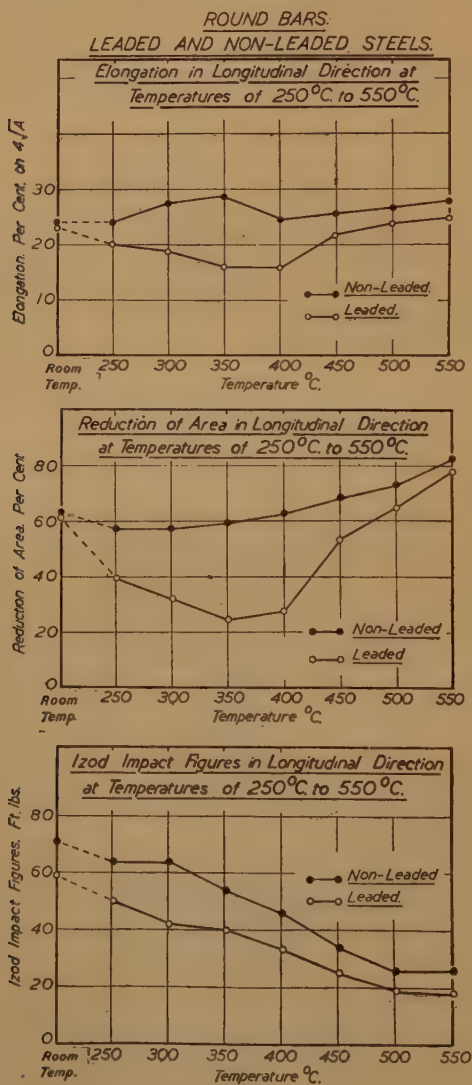


FIG. 4.

temperature is increased from 250° to 500° or 550° C. and increasing values as the temperature is further increased to 600° C. The

impact values of the leaded steel are generally slightly lower than those of the non-leaded steel up to 500° C., but the reverse is the case at 600° C. The values for the two steels are similar at about 24 ft.lb. when tested at 550° C.

The impact figures of transverse specimens of the non-leaded steel fall from 15 ft.lb. at 250° C. to 8 ft.lb. at 500° and remain low up to 600° C. The impact values of the leaded steel are slightly lower than those of the non-leaded steel over the range of temperature from 250° to 600° C.

(b) Tests on Round Bars.

Lengths of $\frac{3}{4}$ -in. dia. bar were oil-quenched from 840° C. and tempered at 650° C. Tensile and impact tests were carried out at temperatures of 250° to 550° C. in 50° intervals. The tensile specimens were strained at a rate of $\frac{1}{24}$ in. per min. up to the maximum stress, then at $\frac{1}{2}$ in. per min. to fracture. The results are recorded in Table IV.

There is no significant difference in the maximum-stress figures between the non-leaded and leaded steels on testing up to 550° C.; both show a gradual decrease as the test temperature is increased from 250° to 550° C.

The elongation, reduction-of-area and Izod impact values are shown graphically in Fig. 4.

The elongation figures for both steels show minimum figures at about 400° C., as in the case of the flat bar material. The values for the leaded steel are lower than those of the non-leaded steel.

In the non-leaded steel the reduction of area increases gradually from 300° to 550° C.; the leaded steel, on the other hand, shows a minimum at 350° C., this value being markedly lower than the corresponding one for the non-leaded steel.

The Izod impact values of both steels decrease gradually as the test temperature is increased from 250° to 550° C., the values for the leaded steel being consistently lower than those of the non-leaded steel.

CREEP TESTS.

Barr-Bardgett creep tests were carried out at 500° C. on specimens machined from $\frac{5}{8}$ -in. dia. bars, oil-quenched from 840° C. and tempered at 650° C. for 1 hr., having the following mechanical properties :

		Non-Leaded.	Leaded.
Max. stress.	Tons per sq. in.	56.8	56.8
Yield stress.	Tons per sq. in.	52.0	52.4
Elongation on 2 in.	%	26.0	24.0
Reduction of area.	%	63.6	61.6
Izod impact value :	Ft.lb.	81, 84, 72	59, 65, 61
	Average	79	62
Barr-Bardgett creep stress value.	Tons per sq. in.	1.7	1.7
1943—ii			GG

The leaded and non-leaded steels had identical Barr-Bardgett creep stress values at 500° C.

DAMPING CAPACITY.

Measurements of damping capacity were made on a Cambridge torsional damping machine on specimens machined from bars heat-treated to approximately 53 and 65 tons per sq. in., respectively. In order to ensure that the stress applied in the damping tests did not exceed the limit of proportionality in torsion, determinations were made of the limit of proportionality in torsion, the following results being obtained :

Steel : Heat treatment:	Non-Leaded.		Leaded.	
	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.
Max. stress, tension. Tons per sq. in.	52.7	66.2	52.8	65.2
Limit of proportionality, torsion. Tons per sq. in.	25.4	29.0	26.1	31.0
Surface shear strain at limit of proportionality	0.00486	0.00557	0.00502	0.00605
Modulus of rigidity. Tons per sq. in.	5230	5200	5200	5120

The results of the damping tests are shown in Figs. 5 and 6.

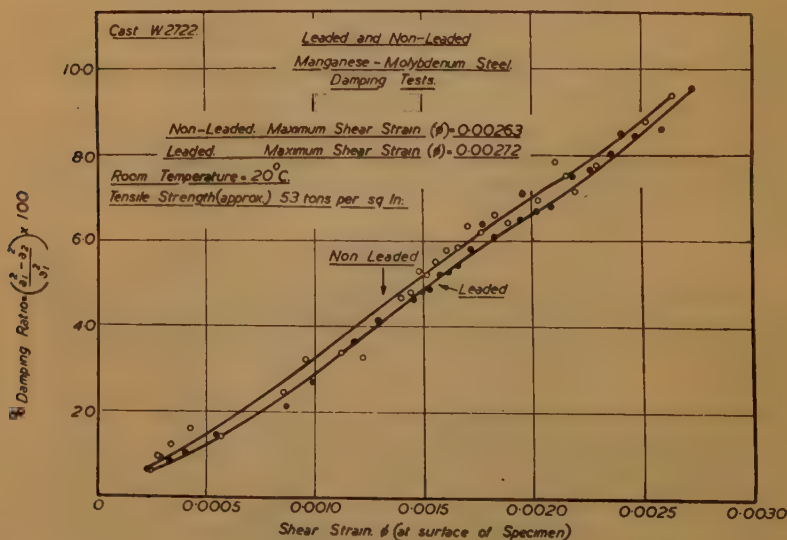


FIG. 5.

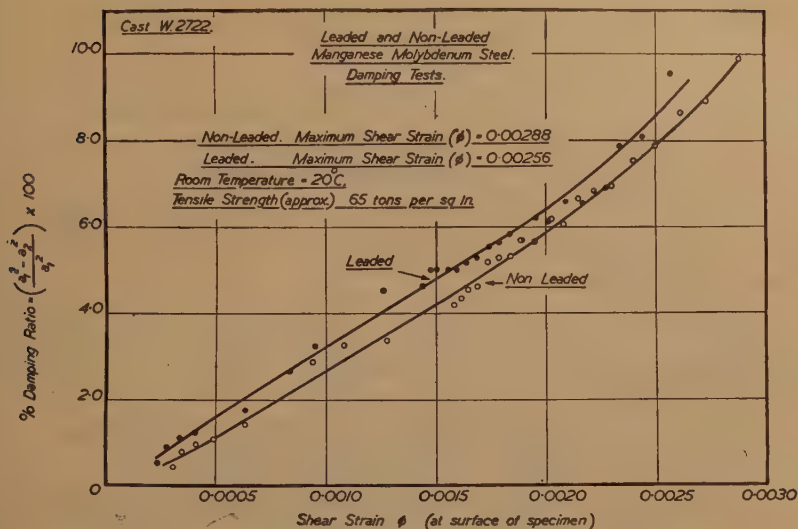


FIG. 6.

The difference in damping capacity of the two steels is practically negligible when treated either to 53 or 65 tons per sq. in., although at the higher tensile strength the leaded steel has a slightly higher damping capacity than the non-leaded steel.

Some doubts have been expressed as to whether the Cambridge machine provides either absolute or even reliable determinations of damping capacity. All that is claimed in this short statement is that the results are comparable and that, in our experience, the machine provides results with a degree of reproducibility which justifies the comparison stated herein.

FATIGUE TESTS.

Rotating cantilever (Wöhler) and alternating direct stress (Haigh) fatigue tests were carried out on both steels. Both plain and notched specimens were used in the tests on the Wöhler machine, but plain specimens only were tested in the Haigh machine. Tensile and impact specimens treated along with the fatigue specimens to tensile-strength values of approximately 53 and 65 tons per sq. in. gave the results collected in Table V.

The results of the fatigue tests are recorded in an Appendix and are shown graphically in Figs. 7 to 10. A summary of the results is given in Table VI.

In the rotating-cantilever tests the plain and notched specimens of both steels treated to the higher tensile strength and the notched

TABLE V.—Round Bars. *Mechanical Properties of Material used for Fatigue Tests.*

Steel :	Non-Leaded.		Leaded.	
Test material :	$\frac{3}{4}$ -in. dia. Bar for (Wöhler) Rotating Cantilever Fatigue Test.			
Heat treatment :	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.
Max. stress. Tons per sq. in.	54.6	66.1	56.4	65.9
Yield stress. Tons per sq. in.	52.7	61.8	54.0	60.1
Elongation on 2 in. %	24.5	20.5	24.0	19.0
Reduction of area. %	63.6	59.2	59.2	57.2
Izod impact value :				
Ft.lb.	67, 73, 79	54, 59, 50	54, 58, 58	48, 47, 46
Average	73	54	57	47
Test material :	$\frac{1}{2}$ -in. dia. Bar for (Haigh) Alternating Direct Stress Fatigue Test.			
Heat treatment :	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.	O.Q. 840° C., T. 660° C. 2 hr.	O.Q. 840° C., T. 620° C. 1 hr.
Max. stress. Tons per sq. in.	52.7	66.2	52.8	65.2
Yield stress. Tons per sq. in.	50.2	63.6	47.1	62.0
Elongation on 2 in. %	26.5	21.0	24.0	20.5
Reduction of area. %	66.0	59.2	61.6	57.2
Izod impact value :				
Ft.lb.	90, 87, 81	51, 52, 47	72, 70, 74	41, 42, 42
Average	86	50	72	42

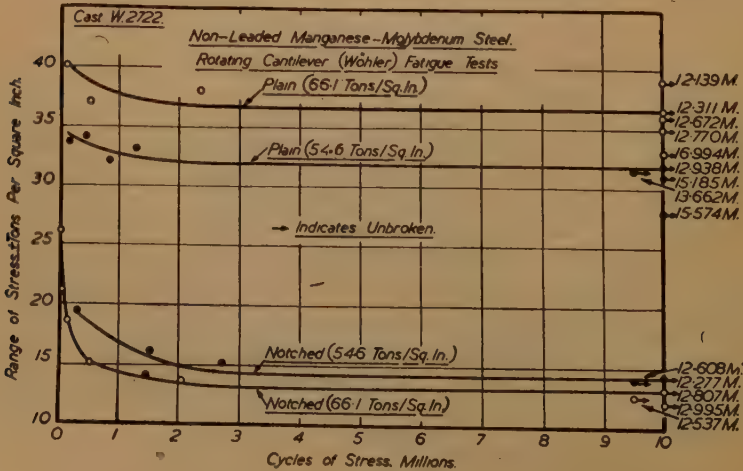


FIG. 7.

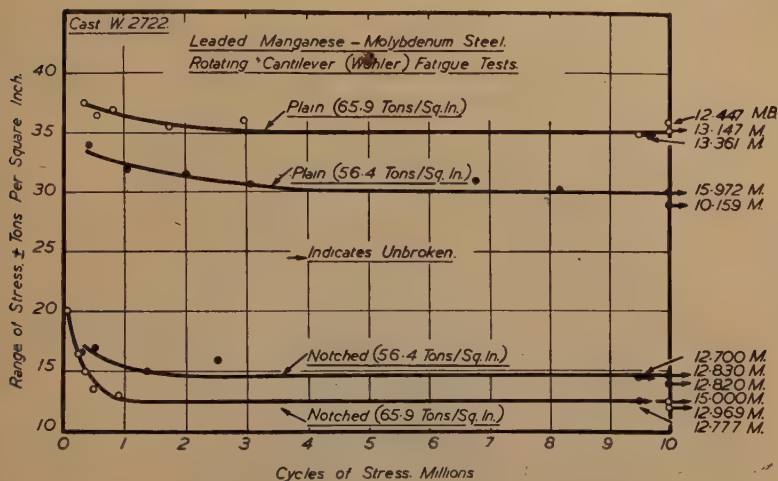


FIG. 8.

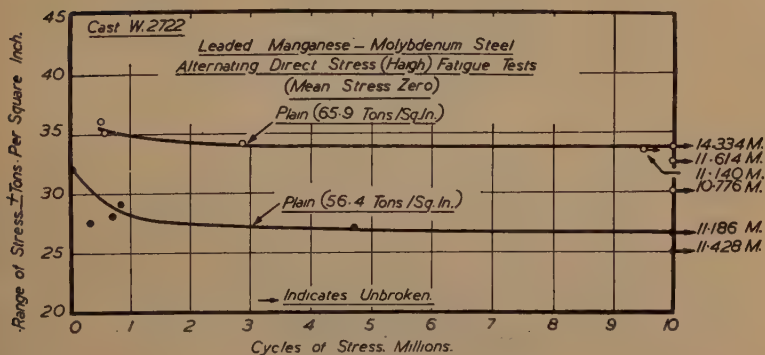


FIG. 9.

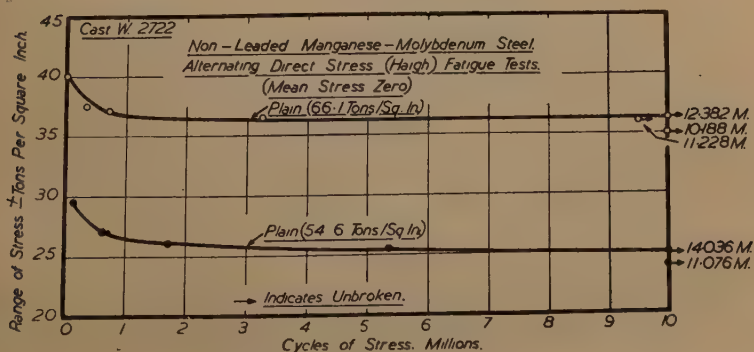


FIG. 10.

specimens treated to the lower tensile strength show similar values respectively for the fatigue ratios. The plain specimens of the non-lead steel treated to the lower tensile strength have a slightly higher fatigue ratio than the corresponding specimens of the lead steel.

TABLE VI.—Round Bars. Summary of Fatigue Tests.

	Rotating Cantilever (Wöhler) Tests.							
Quality :	Non-Leaded (LL).				Leaded (KK).			
Type of specimen :	Plain, P.	Notched, N.	Plain, P.	Notched, N.	Plain, P.	Notched, N.	Plain, P.	Notched, N.
Maximum strength (MS). Tons per sq. in. . . .	54.64		66.08		56.44		65.92	
Limiting fatigue stress (LFS). \pm tons per sq. in. .	31.75	13.75	36.6	13.1	30.0	14.75	35.25	12.5
Fatigue ratio, MS/LFS	0.58	0.25	0.55	0.20	0.53	0.26	0.54	0.19
Notch sensitivity, (P - N)/P . . .	0.57		0.64		0.51		0.65	
	Alternating Direct Stress (Haigh) Tests. Mean Stress zero.							
Quality :	Non-Leaded.				Leaded.			
Type of specimen :	Plain, P.		Plain, P.		Plain, P.		Plain, P.	
Maximum strength (MS). Tons per sq. in. . . .	52.68		66.24		52.84		65.2	
Limiting fatigue stress (LFS). \pm tons per sq. in. .	25.0		36.25		26.5		33.75	
Fatigue ratio, MS/LFS	0.47		0.55		0.50		0.52	
Ratio of Haigh LFS to Wöhler LFS	0.79		0.995		0.89		0.96	

The notch sensitivity of the higher-tensile steels is similar, whilst at the lower tensile strength the non-lead steel is slightly more notch-sensitive than the lead steel.

The direct-stress fatigue-test results show a slightly higher fatigue ratio for the non-lead steel than for the lead steel treated to the higher tensile strength, but the reverse is the case for the specimens treated to the lower tensile strength. The differences are, however, comparatively small.

MACHINABILITY.

The principal object of this paper is to deal with properties other than machinability, although it should perhaps have been stated in



(a) Leaded Steel.
FIG. 11.—Samples of Swarf from the Leaded and Non-Leaded Manganese-Molybdenum Steels.
(b) Non-Leaded Steel.

the introduction that the first objective of adding lead is to improve machinability.

A good deal of both laboratory and, what is more important, production data are available on this point, and, so far as the author is aware, no difference of opinion exists as to the improvement brought about in the machinability of this type of steel by the introduction of lead.

The following represents one set of laboratory tests in confirmation of the improved machinability.

Standard Losenhausen machinability tests were carried out on bars heat-treated, respectively, to approximately 57 and 65 tons per sq. in. tensile strength, with the following results :

Steel : Heat Treatment :	Non-Leaded.		Leaded.	
	O.Q. 840° C., T. 650° C.	O.Q. 840° C., T. 590° C.	O.Q. 840° C., T. 650° C.	O.Q. 840° C., T. 590° C.
Brinell hardness . . .	259	295	258	297
Machinability index . .	242	243	175	175

The leaded steel has considerably better machinability than the non-leaded steel to the extent of 38% for the specimens of both higher and lower tensile strength, the machinability indices being independent of the hardness in each case.

A photograph of typical samples of swarf from the leaded and non-leaded steels is shown in Fig. 11. There is a very pronounced difference in the two samples as regards length, that of the leaded steel being very much shorter than that of the non-leaded steel.

SUMMARY.

The following summarises the results of a comprehensive series of tests carried out on material from an ingot of leaded and of non-leaded manganese-molybdenum steel with the object of determining the effect of the addition of lead (0.19%) on the mechanical properties, including machinability, of this quality of steel.

Preliminary tests showed that the leaded steel was free from lead segregation and had a slightly coarser grain size than the non-leaded steel. Further, as judged by the Jominy depth-hardenability tests, the non-leaded steel had greater hardenability, as regards both maximum hardness and depth of hardening, than the leaded steel.

Tests on Flat Bars.

(1) The difference in the effect on the tensile and impact properties of water-quenching compared with oil-quenching is negligible for both steels at room temperature.

(2) The maximum-stress, elongation and reduction-of-area values show only comparatively slight differences between the leaded and the non-leaded steel in both the longitudinal and the transverse directions.

(3) Both steels undergo a marked but normal reduction in elongation and in reduction of area in the transverse compared with the longitudinal direction.

(4) The Izod impact figures of the non-lead steel are, in general, slightly superior to those of the lead steel in the two directions. The figures obtained on transverse specimens are low for both steels.

(5) The maximum-stress figures of the longitudinal and transverse specimens of the non-lead steel and lead steels are respectively similar, and all show a gradual decrease as the test temperature rises from 300° to 450° C.

(6) The elongation figures of the longitudinal and transverse specimens of both steels are at a minimum in the tests at 400° C. within the range from 300° to 450° C. The values for the lead steel are appreciably lower than those for the non-lead steel, particularly in the transverse direction.

(7) In the longitudinal and transverse specimens of the non-lead steel the reduction-of-area value increases as the test temperature is raised from 300° to 450° C.; the lead steel gives minimum values at 400° C. The figures for the lead steel are markedly lower than those of the non-lead steel, particularly in the tests on transverse specimens and especially at 400° C.

(8) In the range of temperature from 250° to 550° C. the Izod impact figures of the non-lead steel in both the longitudinal and transverse directions are slightly superior to those of the lead steel.

Tests on Round Bars Heat-Treated within the Range 53–65 tons per sq. in. Tensile Strength.

(1) The maximum stress and limit of proportionality of the lead steel and non-lead steels are respectively similar.

(2) The yield-stress values of the lead steel tend to be lower than those of the non-lead steel.

(3) The ductilities of the two steels, as measured by the elongation and the reduction of area, are similar, the general tendency being, however, for the lead steel to be slightly less ductile than the non-lead steel.

(4) The notched impact toughness of the lead steel is slightly less than that of the non-lead steel.

(5) The modulus-of-elasticity figures of the non-lead steel are practically the same irrespective of the tensile strength, whilst those of the lead steel increase progressively with increasing tensile strength. At 56.8 tons per sq. in. tensile strength the figures for the lead steel are similar to those of the non-lead steel.

(6) There is no significant difference in the maximum-stress figures between the non-lead steel and lead steels on testing up to 550° C.

(7) The elongation figures for both steels show minima at about 400° C., as in the case of the flat bar material. The values for the leaded steel are lower than those of the non-leaded steel.

(8) In the non-leaded steel the reduction of area increases gradually as the test temperature is increased from 300° to 550° C.; the leaded steel, on the other hand, shows a minimum at 350° C., this being markedly lower than the corresponding value for the non-leaded steel.

(9) The Izod impact values of both steels decrease gradually as the test temperature is increased from 250° to 550° C., the values for the leaded steel being consistently lower than those of the non-leaded steel.

(10) The creep-stress values of the two steels at 500° C., determined by the Barr-Bardgett method, are identical.

(11) The damping capacities of the two steels are practically the same. When treated to 65 tons per sq. in. tensile strength the leaded steel has, however, a slightly higher damping capacity.

(12) Rotating cantilever fatigue tests on plain specimens of both steels treated to (approximately) 65 tons per sq. in. tensile strength give similar values for the fatigue ratio. When treated to the lower tensile strength of (approximately) 55 tons per sq. in. the value for the fatigue ratio of the non-leaded steel is slightly higher than that of the leaded steel.

(13) Rotating cantilever fatigue tests on notched specimens of the two steels yield similar values for the fatigue ratio.

(14) Notch-sensitivity determinations on rotating cantilever specimens show similar values for the two steels when treated to (approximately) 65 tons per sq. in., but the non-leaded steel is slightly more notch-sensitive than the leaded steel when treated to the lower tensile strength of (approximately) 55 tons per sq. in.

(15) Direct-stress fatigue test results indicate a slightly higher fatigue ratio for the non-leaded than the leaded steel treated to (approximately) 65 tons per sq. in. tensile strength, but the reverse is the case for the specimens treated to 53 tons per sq. in. tensile strength. The differences are, however, comparatively small.

(16) The leaded steel has a 38% better machinability than the non-leaded steel when the steels are treated to 57 and 65 tons per sq. in. tensile strength as judged by the standard Losenhausen test.

(Appendix follows.)

APPENDIX.—*Rotating-Cantilever and Direct-Stress Fatigue Test Results.*

TABLE VII.

Quality : Non-leaded.
Tensile strength : 54·6 tons per sq. in.
Machine : Rotating cantilever (Wöhler).
Type of specimen : Plain.
Dia. of specimens :
0·300 { +0·0000 in.
 -0·0000 in.

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
34·0	0·453 B
33·5	0·181 B
33·0	1·293 B
32·0	0·844 B
31·75	12·938 U
31·5	13·662 U
31·0	15·185 U
28·0	12·574 U
Limiting fatigue stress : ± 31·75 tons per sq. in.	

* B = broken; U = unbroken.

TABLE IX.

Quality : Non-leaded.
Tensile strength : 66·1 tons per sq. in.
Machine : Rotating cantilever (Wöhler).
Type of specimen : Plain.
Dia. of specimens :
0·300 { +0·0000 in.
 -0·0000 in.

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
40·0	0·111 B
39·0	12·139 U
38·0	2·387 B
37·0	0·534 B
36·6	12·311 U
36·0	12·672 U
35·0	12·770 U
33·0	16·994 U
Limiting fatigue stress : ± 36·6 tons per sq. in.	

* B = broken; U = unbroken.

TABLE VIII.

Quality : Non-leaded.
Tensile strength : 54·6 tons per sq. in.
Machine : Rotating cantilever (Wöhler).
Type of specimen : Notched ($\frac{3}{8}$ -in. Whitworth form).
Dia. of specimens :
0·335 { +0·0000 in. } at top of
 -0·0005 in. } notch.
0·295 { +0·0020 in. } at bottom
 -0·0000 in. } of notch.

Range of Stress. ± tons per sq. in. (Calculated on Cross-Section at Bottom of Notch.)	Cycles of Stress.* Millions.
19·2	0·321 B
16·0	1·557 B
15·1	2·789 B
14·0	1·491 B
13·75	12·277 U
13·5	12·608 U
12·5	12·537 U
Limiting fatigue stress : ± 13·75 tons per sq. in.	

* B = broken; U = unbroken.

TABLE X.

Quality : Non-leaded.
Tensile strength : 66·1 tons per sq. in.
Machine : Rotating cantilever (Wöhler).
Type of specimen : Notched ($\frac{3}{8}$ -in. Whitworth form).
Dia. of specimens :
0·335 { +0·0000 in. } at top of
 -0·0000 in. } notch.
0·295 { +0·0030 in. } at bottom
 -0·0010 in. } of notch.

Range of Stress. ± tons per sq. in. (Calculated on Cross-Section at Bottom of Notch.)	Cycles of Stress.* Millions.
26·0	0·034 B
21·0	0·071 B
18·5	0·145 B
15·0	0·553 B
13·5	2·083 B
13·1	12·807 U
12·0	12·995 U
Limiting fatigue stress : ± 13·1 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XI.

Quality : Leaded.
 Tensile strength : 56.4 tons per sq. in.
 Machine : Rotating cantilever (Wöhler).
 Type of specimen : Plain.
 Dia. of specimens :
 0.300 { +0.0000 in.
 -0.0000 in.

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
34.1	0.424 B
31.8	1.043 B
31.5	2.026 B
31.1	6.797 B
30.7	3.072 B
30.25	8.177 B
30.0	15.972 U
29.0	10.159 U
Limiting fatigue stress : ± 30.0 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XIII.

Quality : Leaded.
 Tensile strength : 65.9 tons per sq. in.
 Machine : Rotating cantilever (Wöhler).
 Type of specimen : Plain.
 Dia. of specimens :
 0.300 { +0.0000 in.
 -0.0000 in.

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
37.5	0.362 B
36.9	0.820 B
36.5	0.560 B
36.0	12.447 B
36.0	2.978 B
35.5	1.754 B
35.25	13.147 U
35.0	13.361 U
Limiting fatigue stress : ± 35.25 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XII.

Quality : Leaded.
 Tensile strength : 56.4 tons per sq. in.
 Machine : Rotating cantilever (Wöhler).
 Type of specimen : Notched.
 Dia. of specimens :
 0.335 { +0.0000 in. } at top of
 -0.0005 in. } notch.
 0.295 { +0.0000 in. } at bottom
 -0.0000 in. } of notch.

Range of Stress. ± tons per sq. in. (Calculated on Cross-Section at Bottom of Notch.)	Cycles of Stress.* Millions.
17.0	0.534 B
16.5	0.292 B
16.0	2.540 B
15.0	1.383 B
14.75	12.830 U
14.5	12.760 U
14.0	12.820 U
12.5	12.777 U
Limiting fatigue stress : ± 14.75 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XIV.

Quality : Leaded.
 Tensile strength : 65.9 tons per sq. in.
 Machine : Rotating cantilever (Wöhler).
 Type of specimen : Notched ($\frac{3}{8}$ -in. Whitworth form).
 Dia. of specimens :
 0.335 { +0.0005 in. } at top of
 -0.0000 in. } notch.
 0.295 { +0.0030 in. } at bottom
 -0.0000 in. } of notch.

Range of Stress. ± tons per sq. in. (Calculated on Cross-Section at Bottom of Notch.)	Cycles of Stress.* Millions.
20.1	0.076 B
16.5	0.255 B
15.0	0.376 B
13.5	0.502 B
13.0	0.917 B
12.5	15.000 U
12.0	12.969 U.
Limiting fatigue stress : ± 12.5 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XV.

Quality : Non-leded.
 Tensile strength : 52.7 tons per sq. in.
 Machine : Alternating direct stress (Haigh) (mean stress, zero).
 Type of specimen : Plain.
 Dia. of specimens :
 $0.140 \begin{cases} +0.0015 \text{ in.} \\ -0.0000 \text{ in.} \end{cases}$

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
29.0	0.140 B
27.0	0.626 B
26.0	1.726 B
25.5	5.380 B
25.0	14.036 U
24.0	11.076 U
Limiting fatigue stress : ± 25.0 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XVII.

Quality : Leaded.
 Tensile strength : 52.8 tons per sq. in.
 Machine : Alternating direct stress (Haigh) (mean stress, zero).
 Type of specimen : Plain.
 Dia. of specimens :
 $0.140 \begin{cases} +0.0005 \text{ in.} \\ -0.0000 \text{ in.} \end{cases}$

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
32.0	0.046 B
29.0	0.844 B
28.0	0.702 B
27.5	0.316 B
27.0	4.726 B
26.5	11.186 U
25.0	11.428 U
Limiting fatigue stress : ± 26.5 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XVI.

Quality : Non-leded.
 Tensile strength : 66.2 tons per sq. in.
 Machine : Alternating direct stress (Haigh) (mean stress, zero).
 Type of specimen : Plain.
 Dia. of specimens :
 $0.140 \begin{cases} +0.0000 \text{ in.} \\ -0.0010 \text{ in.} \end{cases}$

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
40.0	0.022 B
37.5	0.352 B
37.0	0.706 B
36.5	3.248 B
36.25	12.382 U
36.0	11.228 U
35.0	10.188 U
Limiting fatigue stress : ± 36.25 tons per sq. in.	

* B = broken; U = unbroken.

TABLE XVIII.

Quality : Leaded.
 Tensile strength : 65.2 tons per sq. in.
 Machine : Alternating direct stress (Haigh) (mean stress, zero).
 Type of specimen : Plain.
 Dia. of specimens :
 $0.140 \begin{cases} +0.0000 \text{ in.} \\ -0.0000 \text{ in.} \end{cases}$

Range of Stress. ± tons per sq. in.	Cycles of Stress.* Millions.
36.0	0.512 B
35.0	0.586 B
34.0	2.892 B
33.75	14.334 U
33.5	11.140 U
32.5	11.614 U
30.0	10.776 U
Limiting fatigue stress : ± 33.75 tons per sq. in.	

* B = broken; U = unbroken.

[This paper was discussed jointly with the preceding one by L. Northcott and D. McLean on "The Structure and Segregation of Two Ingots of Ingot Iron, one containing Lead."]

JOINT DISCUSSION.

The papers by L. Northcott and D. McLean on "The Structure and Segregation of Two Ingots of Ingot Iron, One Containing Lead" and by T. Swinden on "Leaded Manganese-Molybdenum Steel" were discussed jointly.

Mr. W. B. WRAGGE (Ledloy Ltd., London): I regard it as an honour to be asked to open the discussion on a subject which I have had very much at heart for the last four or five years. Incidentally, my connection with lead-bearing steel has been in the main associated with the assessment of the improved machinability ascribed to lead-bearing steel and the commercial utilisation of that improvement. I am very pleased to see that two papers outlining certain properties of lead-bearing steels have been presented to this Institute at a time when very considerable interest has been aroused in the utility of these lead-bearing steels for machining purposes.

The authors of both these papers apparently assume that lead-bearing steels show materially improved machining characteristics. The following table of our test figures on ingot-iron billets, lead-bearing and lead-free, show energy consumptions substantially in accordance with Dr. Northcott's quoted figures; the values were obtained on a similar Oxford Airey type machine:

Conditions of Test: Same as in Table III., p. 436 P.

Material.	Leaded (0.19% Lead).	Lead-Free.
Ingot iron, rim	2.76×10^4 ft. lb. per cu. in.	3.78×10^4 ft. lb. per cu. in.
Billets, core	2.45×10^4 " "	3.18×10^4 " "

It is worth noting that Dr. Northcott's figures indicate that the energy consumption decreases at the rim with increasing lead content. Dr. Swinden's paper refers to Losenhausen machinability tests, indicating that heat-treated lead-bearing manganese-molybdenum steel had better machinability of the order of 38%. Machine-shop production data on this class of steel indicate an average increase in production of about 40%, making use of increased cutting speed or feed, or both. A typical case is given below:

Material: Manganese-Molybdenum High-Tensile Steel, Brinell Hardness Number 260-270, as Forgings.

Operation.	Conditions for Leaded Steel.	Cycle Time.	
		Leaded.	Lead-Free.
1st; rough turn and face	Increased feed and speed	25 min.	35 min.
2nd; rough turn and bore		30 " "	45 " "
3rd; thread mill	No change	Tool life increased twelve-fold.	

Energy consumptions determined by means of the Oxford Airey type of machine used by Dr. Northcott and Mr. McLean show a 17% advantage in favour of the leaded steel at a hardness of 250–270 in the tempered condition. The relation between energy consumption values and other methods of assessing machinability has been discussed in a recent article. Referring to the paper by Dr. Northcott and Mr. McLean, it will be of interest to examine whether the addition of a heavy, presumably immiscible metal, such as lead, to steel, which metal might associate with the non-metallics, preferably the metalloids, would in any way affect the degree of segregation of these metalloids. It will be observed that (1) the addition of 53 lb. of lead to the ingot will probably reduce the degree of superheat of the metal by about 7° C. and so increase the viscosity. (2) The drop in lead content at the rim (*see* Fig. 2) is likely to be due in part to loss of lead as vapour carried off by carbon monoxide. It is possible that the increase of lead content from top to bottom of the rim (Table I.) is due to the same cause. (3) The average ratio of lead to sulphur content at the core (*see* Fig. 2) is 5.4, whereas at the rim the ratio is 9.6. An examination of a leaded ingot iron at the billet stage some two years ago yielded ratios of 7.7 at the core and 10.9 at the rim. (4) It has been stated that it is characteristic of rimmed steels of the ingot-iron type that sulphur tends to segregate vertically at the core, possibly owing to the flotation of immiscible separated complex sulphides. Lead-bearing ingot *TTP*, *see* Table I., shows a greater rate of sulphur increase at the core than ingot *TTQ*. If lead were in the main associated with the complex sulphides, and bearing in mind the probably greater initial viscosity of the lead-bearing melt, one would expect the opposite to have occurred. The above observations lead me to postulate that the lead in ingot *TTP* can be associated with the sulphides to only a minor degree, and that the mechanism of variation of lead content across the section will only in a very small degree be similar to that of sulphur segregation.

Would Dr. Northcott and Mr. McLean describe the micro-chemical analysis method employed for the estimation of lead, and would they kindly confirm that the rolled specimens subjected to annealing at 950° C. (*see* p. 436 P) were obtained from the rim. Did they observe the depth of the chill crystal zone and whether or not it contained lead.

There are only two features of Dr. Swinden's paper which I care to discuss, first in connection with the observed peculiar rise in value of modulus of elasticity with increase in hardness (*see* Table II., p. 444 P), and secondly the peculiar fall in ductility and notched toughness, showing a maximum difference as compared with lead-free steel at about 350–400° C.

The following experimental results confirm the observations on the change of elastic modulus :

Material: Carbon, 0.36%; Manganese, 1.61%; Silicon, 0.196%; Molybdenum, 0.37%; Lead, 0.19%. Size, $\frac{1}{2}$ in. dia. Treatment, normalised at 910° C. for 2 hr., O.Q. 840° C.

Tempering Temp. (1 hr.). ° C.	Brinell Hardness Number.	Modulus of Elasticity. Tons per sq. in.
500	316	12,300
550	293	12,900
600	255	13,200
650	219	12,900

A large number of tests would, however, be required to provide final conclusive evidence. It is of interest to observe that, while Dr. Swinden's figures for the elastic modulus show an increase in the leaded steel tempered at 620° C. (*see* Table II.), the values of modulus of rigidity after tempering at 620° C. (p. 450 P) indicate a small drop in the case of the leaded specimen.

Surprising variations in Poisson's ratio and in change of density under stress, calculated from the above figures, are given below :

	Tempered at 660° C.		Tempered at 620° C.	
	Non-leaded.	Leaded.	Non-leaded.	Leaded.
Poisson's ratio	0.224	0.205	0.230	0.298
Density change at 48 tons per sq. in.	-0.207%	-0.225%	-0.203%	-0.145%

Referring to Dr. Swinden's test figures at elevated temperatures, it would have been of considerable interest to have had available stress-strain diagrams in order to observe the performance of the leaded steel at loads up to and including the maximum stress. Was there any noticeable difference on that side of the stress-strain diagram?

Reduction in notch toughness of leaded steel at elevated temperatures has previously been recorded by Nead, Sims and Harder,¹ the steels examined being mild steels with increased sulphur content and with varying lead additions. Typical Charpy impact values taken from their work are given below :

Steel.	Lead Content. %.	Charpy Impact Test, ft. lb.—	
		At 24° C.	At 315° C.
B	Nil	36.5	30.1
A	0.13	34.8	22.5
C	0.25	29.9	20.5
D	0.26	34.9	27.0

Thanks to the courtesy of Dr. Harder of the Battelle Memorial Institute, and Dr. Nead, Inland Steel Co., I am able to publish data on lead-bearing steels other than manganese-molybdenum steels which show features relating to ductility at elevated temperatures which are akin to those observed by Dr. Swinden (*see* Fig. A). It is interesting to note that both Dr. Swinden's test results and those to which I have just referred indicate a definite recovery of ductility values as the testing temperature increases up to 500–550° C. At

¹ *Metals and Alloys*, 1939, vol. 10, pp. 68, 109:

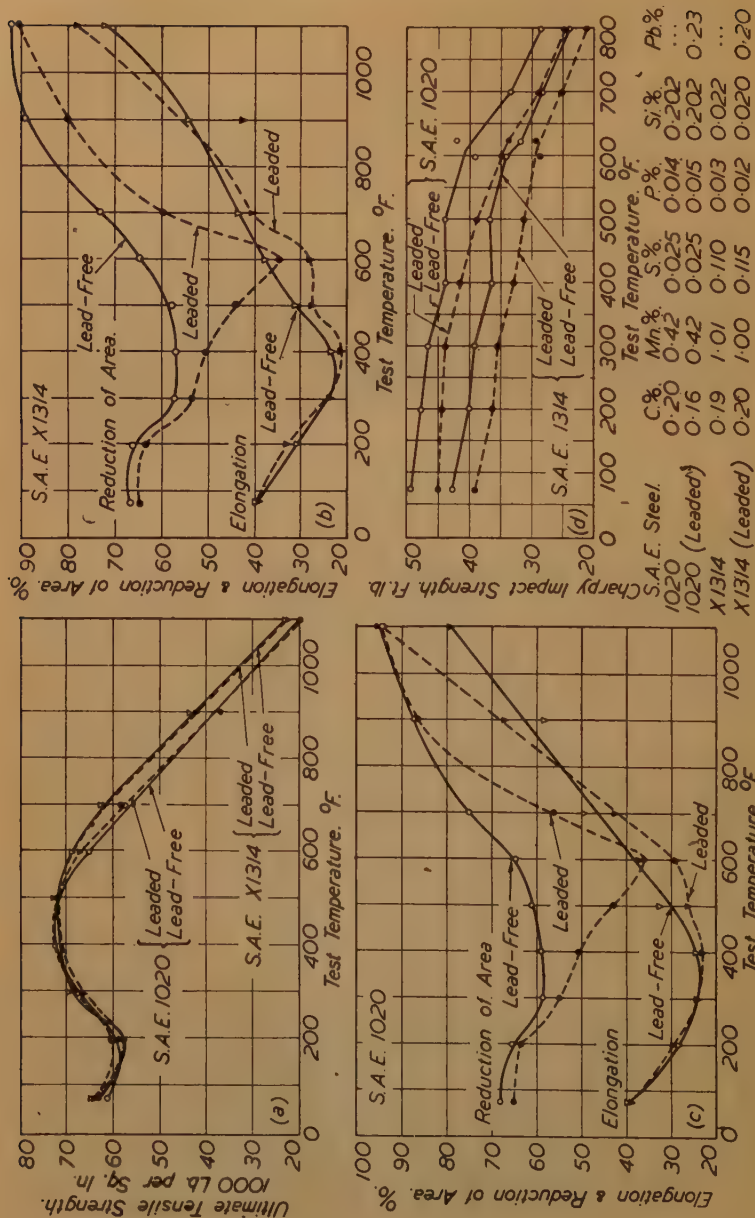


FIG. A.—Graphs of Mechanical Properties of Two Types of Leaded and Non-leaded Steels at Elevated Temperatures in the Normalised Condition.

present I am not in a position to offer any reasonable explanation for the reduced ductility properties of the leaded samples at elevated temperatures nor the recovery of these properties at temperatures towards 550°C . and upwards.

Dr. T. SWINDEN (Member of Council; The United Steel Companies, Ltd., Stocksbridge, near Sheffield): We are indebted to Dr. Northcott and Mr. McLean for their paper, which represents the first publication, so far as I am aware, of a detailed study of the distribution of lead in a rimming-steel ingot. The first point which strikes me is the large amount of lead that was added, which I estimate at about 1.05%, the resulting analyses showing a recovery in the region of 30%. This contrasts with the addition which we are making to killed steel, where the recovery is of the order of 80%. I imagine that when adding lead to ingot iron the fume problem would as a result be much more acute.

Turning to Fig. 2, it is interesting to note the form of the lead-content curve in passing from the outside to the centre of the ingot. As the authors say, this is generally similar to that of sulphur and phosphorus, ignoring the coarser deposits of lead which were found at the extreme base; it is probable that the latter would be largely avoided if the technique of adding lead could be improved so as to enable a smaller total quantity to be added. With regard to the general trend of the curve, however, it is possible that, in addition to the generally accepted view concerning sulphur and phosphorus, there will be a loss of lead during the solidification of the rim under the conditions of solidification known to exist, *i.e.*, comparatively oxidised metal in a state of agitation.

It is important to point out that these comments refer specifically to ingot iron, although they may hold for any type of rimming steel. In the case of solid steel, a complete report on which I hope to present very shortly, the lead certainly does not segregate along the pattern of sulphur and phosphorus. In fact, such variations as exist are usually of the opposite type, with higher lead in the base. It is well known to those making leaded steels that one looks to the bottom end and not to the top end for the discard, to avoid unduly high contents of lead.

I was very interested in the section of the paper dealing with the micro-examination, because there again we are endeavouring by examining ingot sections, in addition to a good deal of work on billet sections, to see further whether we can locate just how this lead does exist; the National Physical Laboratory have some samples for examination with the electron microscope. I do not think that anyone is prepared to say at the moment just how that lead does exist, and, if I may add a comment to that of Mr. Wragge, we too would say from what we have done that there is no evidence that the bulk of the lead is associated with the sulphide inclusions.

Mr. Wragge is in a unique position to contribute information on

machinability, and I look forward very much to the further data that he has promised to provide.¹ He will fill up a quite definite omission in my paper by giving details on machinability, because I chose to concentrate on other properties. It is interesting to note from the present paper that the improvement in machinability by the addition of lead is proportionately greater in the rim (3.58–2.48 ft. lb. per cu. in.) than it is in the core (2.91–2.40 ft. lb. per cu. in). This does indicate that the otherwise bad machining properties of the rim of a rimming steel can be very substantially improved by this addition of lead.

Finally, I have no immediate data on machinability by this particular method, and if the authors could amplify this by giving

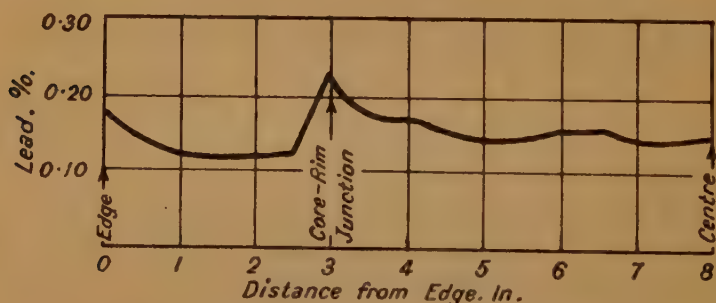


FIG. B.—Lead Content from Edge to Centre of Ingot.

a few comparative figures, under the same conditions of test, for other steels, such as a few of the well-known free-cutting steels or other standard steels, it would help me considerably in comparing these figures with our own. We have masses of information obtained by the Losenhausen and by certain other tests.

Mr. C. S. GRAHAM (Messrs J. Lysaght, Ltd., Scunthorpe, Lincs.) : The authors of both papers are to be congratulated on placing on record interesting data on leaded steels. I shall, however, confine my remarks to the first paper, as Dr. Swinden's paper has been adequately dealt with by Mr. Wragge.

The primary object of the paper by Dr. Northcott and Mr. McLean is the study of the segregation of lead in rimming steel. In 1938 we made several ingots of ingot iron with lead additions. We did not section them longitudinally; instead, we took a horizontal slice half-way down the ingot, drilled 16 holes from the edge to the centre and tested for lead. The results are shown in Fig. B.

This confirms the authors' findings, *viz.*, the percentage of lead decreases from the edge of the ingot to the junction of the core and

¹ Now incorporated in Mr. Wragge's contribution.

the rim, then suddenly rises and finally falls again to the centre of the ingot.

The authors draw attention to the high copper content in the ingot iron. We found that when lead is added to ingot iron or steel containing copper, a certain amount of the copper is dissolved in the lead. I should expect, if the authors analysed the lead from that particular ingot, that they would find the copper content to be about 0.040%.

The casting conditions given are interesting, but the only casting condition which has any effect on the lead content and its distribution is the temperature, which, unfortunately, has been omitted.

Tests made on the finished product (billets) in 1938 led us to the conclusion that lead additions do not interfere with the rimming reaction. It is rather unfortunate that these two ingots were not tested for oxygen to ascertain whether or not the lead removes any oxygen.

As regards the microstructure, about three years ago we developed a method for the microscopic identification of lead in steel. According to this method the sections are very carefully polished, the lead smear is removed by alcoholic nitric acid and the surface is finally treated with weak alcoholic nitric acid and potassium iodide solutions. Under bright-field illumination no lead iodide is visible, but under dark-field illumination we find particles of yellow lead iodide. After using this method for a short time, however, we found that from a quantitative point of view it has its limitations, because the conversion of lead to lead iodide is always associated with an increase in volume; in other words, the lead iodide particles are larger than the original lead particles which formed the iodide. This method can also be used for macroscopic work and is very useful for identifying lead segregation.

In any paper of this type, which deals with a very low carbon content, the method of analysis of the carbon should be stated. If the carbon percentages of the order of 0.02%, mentioned on pp. 430 P and 432 P, were estimated by the usual gravimetric method, they are of very little scientific value, because the experimental error is much too great. These remarks apply to all steel ingots containing 0.06% or less of carbon.

It will be interesting to learn what experimental error the authors expect from their micro-chemical methods of analysis for carbon. If we take 0.042% carbon as the average of the micro-tests and allow 0.02% for carbon elimination in the moulds owing to the rimming reaction, the carbon content of the steel leaving the furnace should be about 0.06%—which may account for the higher carbon content at the extreme edge of the ingot mentioned on p. 434 P. Unfortunately, the pit sample was not killed with aluminium, and therefore will not show the true carbon content of the steel in the ladle.

Mr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett, Co.

Durham): I am not completely satisfied that the rimmed parts of the two ingots described by Dr. Northcott and Mr. McLean had a columnar structure. The evidence that they advance is based on the effect produced by Stead's reagent, but that solution was originally intended for micro-etching, and its application for a few seconds was then quite sufficient to reveal heterogeneity. Prolonged etching such as would be needed in treating large masses might give an entirely misleading result. Moreover, a cored structure in an ingot generally gives rise to a banded structure in the rolled product which can readily be detected by cupric etching, but I have never been able to discover any banding in the rim portions of billets or plates rolled from ingots of the type dealt with by the authors; the purer outer zones seemed to be quite homogeneous. For these two reasons I am not prepared to accept the conclusion that a columnar structure was present in the ingot until corroboration has been obtained by some other means.

I consider that Dr. Swinden has contributed a paper of much interest and practical value. The only point that I wish to remark on is the fact that the addition of lead to the steel apparently somewhat increased its grain size in the McQuaid test. Now, since the steel without lead gave a No. 7 size I conclude that aluminium had been added, and, if so, I would suggest that some of it had been absorbed, or washed out, by the lead with a consequent coarsening of the grain size. At the temperature of molten steel the solubility of aluminium in lead is reported to be about 7%, so that an appreciable washing action in the steel might conceivably occur when the lead was added. That idea has set me thinking in another direction. The presence of tin in steel can be definitely harmful. For instance, it can cause severe red-shortness in mild steel when in tension at about 850° C., and I wonder whether that trouble could be eliminated by the addition of lead, in which tin is, of course, very soluble.

As to the manner in which the lead is retained by the solid steel no one at present knows. It does not seem to be strongly held, for when a section of leaded steel is heated at about 400° C. in a neutral atmosphere the lead oozes out and forms droplets on the surface. These droplets are easily flattened into cakes, and I have found that these cakes are blackened by a 10% solution of chromic acid, with the result that they are then unattacked by ordinary etching reagents. But when I applied that treatment to a specimen of dead soft leaded steel in the as-rolled condition I was unable to detect any black particles of lead even under the oil-immersion lens.

Mr. W. W. STEVENSON (The United Steel Companies, Ltd., Stocksbridge, near Sheffield): I have read these papers with great interest. On the paper by Dr. Northcott and Mr. McLean I should like to follow up Mr. Graham's remarks on chemical analysis, particularly from the viewpoint of examining rimming steel rather than leaded steel. The authors state, in dealing with chemical analysis,

that "the carbon, silicon and manganese contents are so very low that segregation of these elements is virtually absent," but if one looks at Table II., I do not think one would find that this is so; under "carbon" values of 0.05%, 0.03%, 0.083%, 0.026%, 0.051% and so on are reported for various positions in the ingots.

The authors also refer to Dr. Binnie's excellent work and to his calculations in connection with the hypothesis of Hultgren and Phragmén. We, at Stocksbridge, are in substantial agreement with Dr. Binnie's figures in respect to the balanced composition. His main conclusion was that the pit-sample carbon results of most investigators were too low; and here, to my mind, is an excellent further example in support of that conclusion. I do not think that this pit sample at 0.02% of carbon can possibly be right; we would put it at 0.04–0.045% from the figures in Table II. How that pit sample was analysed is not stated; probably it was done in the laboratory of the concern producing the ingot; but I would ask the authors to check these carbon figures, and it would be very interesting to have the oxygen results also, as Mr. Graham suggested. We would say that this material probably had about 0.055% of oxygen in the pit sample, and probably about 0.025% in the mid-rim and about 0.045% in the mid-core. In other words, this is an excellent example of a low-carbon, comparatively high-oxygen rimming steel, and the further investigation of it, in particular checking up the figures in Table II. and if possible the pit sample as well, would be valuable.

Mr. J. WOOLMAN (Brown-Firth Research Laboratories, Sheffield): These are two very interesting papers. The data which they contain afford us food for thought, and there are some results in both of them about which I should like to ask the authors one or two questions.

In the paper by Dr. Northcott and Mr. McLean there are certain anomalies in the distribution of the elements, and particularly the lead distribution, which require a certain amount of explanation. For example, the lead is highest at the bottom outside of the ingot, where figures as high as 0.71% are reported, whereas the general average of the ingot appears to be somewhere about 0.3–0.35%. That is rather strange, because at the bottom outside of the ingot one would expect to get rather the average of the ingot, on account of the very rapid chilling effect there; one wonders where the rest of the lead goes to.

I am also interested in the curves showing the lead distribution across the ingot, which seem to suggest that the lead segregation is caused by the same phenomena as that of sulphur and phosphorus. What does this mean? Does it mean, for example, that lead has a limited solubility in steel at very high temperatures, or does it mean that it segregates owing to the fact that it combines with the sulphur, or possibly oxygen, in the steel?

It has been pointed out to me that there is a difference in the sulphur contents of the two steels, although they were made from the same melt; the sulphur in the leaded steel is of the order of 0.04–0.09%, whereas in the non-leaded steel it is something like 0.02–0.07%. I cannot quite understand the reason for the difference. Incidentally, why does one speak of “leaded” and “non-leaded” steels? One does not refer to “nickelled” steels or “coppered” steels. Why do not we say “lead” steels?

Dr. Swinden's paper contains a mass of very useful data. Does he think that the reduction in ductility at high temperatures is really responsible for the free-cutting properties induced by the lead addition. It is usually considered that the free-cutting properties are probably due to the lubricating action of the lead, but it seems to me possible to provide an alternative explanation. During the machining operation the surface being machined is heated and the author has shown that at elevated temperatures the ductility of the lead steel is considerably reduced below that of the non-lead steel. It strikes me that this lower ductility, particularly in the transverse direction, may be responsible for the free-cutting qualities.

CORRESPONDENCE.

Dr. DAVID BINNIE (Lancashire Steel Corporation, Ltd., Irlam, near Manchester) wrote: The leaded and the non-leaded rimming-steel ingots dealt with in the paper by Dr. Northcott and Mr. McLean were the fifth pair of ingots teemed and should have given a comparison of the effect, if any, of lead on the rimming action.

Both ingots rimmed well, but from the analyses in Table II. the leaded ingot would seem to have been the quieter one, a point which is also borne out by inspection of the sulphur prints in Figs. 4 and 5.

The core of the lead-free ingot contains many more blow-holes, just inside the outer portions of the core.

One outstanding analytical difference between the two ingots lies in the phosphorus analysis. At the outside edge the phosphorus percentages agree closely, but, on passing into the ingot, the leaded ingot at all other positions in Table II. contains a lower percentage of phosphorus than does the partner ingot. The non-leaded ingot contains, say, 50% more phosphorus than does the leaded one. The analysis in Table I. does not show this discrepancy; perhaps the authors would explain the reason for the analytical difference in phosphorus between the leaded and the non-leaded ingots as shown in Table II.

AUTHORS' REPLIES.

Dr. NORTHCOTT (in verbal reply): I should like to thank all those who have contributed to the discussion. I am glad that Mr. Wragge in general substantiates our machinability results from his own experience. On the question of the existence of the lead as sulphide or otherwise, I think there can be no doubt that much of the lead is not present as sulphide—some of it may be, but most of it is not. One pointer to that is the fact that in the leaded ingot (or the lead ingot, as Mr. Woolman would have it) there is no greater proportion of sulphides or sulphide deposits than in the lead-free ingot, as far as could be seen from microscopical examination.

On the question of the "streaks," Mr. Wragge was correct in assuming that those streaks were found on material taken from the rim. I should like to call attention to a Swedish paper¹ on a method of etching which is probably identical with the one mentioned by Mr. Graham; it has the disadvantage that the proportion of constituent present as shown by the etching reagent is greater than that actually present. It is stated that the elongated form of the lead inclusions after cold-rolling the steel, as well as the coagulation of the particles after annealing at temperatures above the melting point of lead, could be seen in the micrographs.

By the depth of the chill crystal I take it that Mr. Wragge means the small equi-axial crystals near the extreme outer surface. These were not measured, partly owing to the difficulty in determining the true primary structure.

Dr. Swinden says that his own experience is that the proportion of lead lost was considerably less than is indicated in our paper. I am not sure, but a clue might be given to that by the amount of lead in the finished ingots. In our ingots the lead content was over 0.3%; in the ingot described by Dr. Swinden it was about 0.19%. It is possible that the more lead added, the greater is the proportion lost. I agree with Dr. Swinden that the effect of lead is greater on the machinability of samples cut from the rim. I take it that that is due to the fact that the rim has unsatisfactory machining properties as compared with the core; the core is easier to machine, probably owing to its higher sulphur content and possibly carbide as well. There are results available, and I think that some of them have been published, on machinability tests on other types of steels.

I am not sure that I agree with Mr. Graham that lead has no effect on the rimming action. Whether it is that the addition of lead cools the steel, particularly that just going into the mould, or acts as such by lowering the effective casting temperature or increasing the FeO + carbon reaction I do not know, but there is evidence in these two ingots that the leaded ingot has a greater proportion of blow-holes towards the bottom.

I should like to thank Mr. Whiteley for his remarks. I had

¹ A. von Vegesack, *Jernkontorets Annaler*, 1942, vol. 126, No. 12, p. 559.

suspected that after his very considerable experience on the micro-examination of primary structures with the Stead reagent he might object to our use of that reagent to determine the structure on a large ingot. It is true that the etching took not seconds but minutes, the total time of etching being of the order of half an hour. Etching a low-carbon or very pure ingot is very difficult. Normally the primary structure in ingots is developed by some kind of copper reagent, but a normal copper reagent such as Humfrey's, starting with a neutral and going on to an acid solution, does not act very well with low-carbon or pure iron ingots. Such a deep etching gives rise to porosity. We have tried Humfrey's reagent with this steel, and the results confirm the structure which we consider to be the primary structure in these ingots.

I am not sure whether Mr. Stevenson agrees with the conclusions in our paper or disagrees with them. I agree with him that the pit sample gives no very adequate information on the composition and carbon content of the finished steel, and that is why much more delicate methods were gone into and some considerable amount of work was done to try to obtain the right answer. On the question of the oxygen content, am I to assume that Mr. Stevenson or Dr. Swinden is anxious to do our oxygen contents on these ingots? If so, I shall be very glad to accept their kind offers; pressure of other work at the moment prevents my undertaking this investigation.

In reply to Mr. Woolman, the lead distribution was highest at the outside at the bottom. It was still higher at the extreme bottom of the core, but that is normally the material which would be discarded, whereas in the columnar-crystal portion, the rimming portion, it was lead which had been entrapped. With regard to his question about the similarity of the lead distribution to that of sulphur, I can only ask him why it is that the phosphorus distribution is similar to that of, say, carbon or sulphur. All three elements, or four, including the lead, occur in different forms, and as far as our findings go they behave very similarly.

Dr. NORTHCOTT and Mr. McLEAN, in further reply, wrote: In order to deal adequately with the enquiries for further information on the methods of microchemical analysis, a report on the subject has been prepared and will be issued shortly.

It is thought that the relatively low recovery of lead indicated by the analysis, referred to by Dr. Swinden, may be partly due to the lead deposits in the bottom of the ingot not being included in the samples for analysis.

The results of machinability tests on forged steels of different carbon contents, using the Oxford-Airey machine, are given in Kenneford's paper, to which we referred.

In further reply to Mr. Whiteley, we suggest that, with a relatively pure material such as the rim of these soft iron ingots, the dendritic segregation is much smaller than occurs in more normal

steels, so that more prolonged etching is essential to reveal the segregation, especially when the surface finish is less perfect than that of a polished microspecimen. Additionally, the columnar segregation is normal to the rolling plane, so that the deformation of the columnar crystals would tend to mask the banding effect of the rim portion in forged or rolled material.

The difference in the average sulphur and phosphorus contents to which attention is drawn by Mr. Woolman and Dr. Binnie, respectively, is difficult to account for. The analysis samples of each ingot were, however, examined as a batch for segregation, and it is believed that the figures do indicate the degree of segregation in each ingot.

Dr. SWINDEN (wrote in reply): I should like to thank Mr. Wragge for his very valuable contribution. I am obliged to him for calling attention to the modulus-of-elasticity figures, to which I omitted to refer in introducing the paper, but which are distinctly interesting. In the case of the non-leaded steel the modulus was fairly constant at about 12,800 tons per sq. in., while in the case of the leaded steel the modulus (rather curiously, I think) was increased as the tensile strength was increased from 54 to 65 tons per sq. in. I am very interested to hear that he has confirmatory data on that point.

The values given by Mr. Wragge showing a difference in the elastic modulus with hardness are an interesting confirmation of my own data, although the intrinsic agreement between the two sets of tests is not good.

Stress-strain diagrams were not taken in carrying out the tests at temperature.

I purposely avoided any reference to carbon, a point which has been subsequently taken up energetically by Dr. Binnie and Mr. Stevenson, because it is a subject in itself, and I hope to be able to present another short paper on that point which will indicate how important it is to prepare specially the test sample from rimming steel if the carbon is to be fairly representative of the bulk of the cast.

Mr. Whiteley's contributions are always interesting. His suggestion that lead might possibly wash some aluminium out, and that that is the explanation of the grain size, is interesting, and perhaps gives us a line on what he thinks about the effect of aluminium, because it would indicate that he considers that aluminium in solution is at least a factor in controlling grain size—though perhaps I ought not to put words into his mouth to that extent. The phenomenon of lead oozing out on reheating is, of course, well known, and is the basis of the exudation test which has to be passed in selling this steel. We have studied that very carefully, and also done an extensive piece of work on the chemical separation of inclusions in order to get more information on this

very point of whether the lead is with the inclusions or not. As I indicated before, my opinion at the moment is that it is not, but on the mechanism of the lead oozing out we have actually taken cinema films at high temperatures which show the lead coming out.

Whether an addition of lead will inhibit the effect of tin, or tin plus copper, in this adverse effect on high-tensile properties I do not know. That, again, is a very interesting thought. In a paper which is under preparation it is shown that there is no doubt about the effect of tin and the additive effect of copper in this particular way. It is interesting, in that it is in the high-tensile test that one can differentiate between casts which are satisfactory and unsatisfactory in the form, say, of hot-flanging boiler plate; but the addition of lead to inhibit that is a rather drastic remedy.

There is no mystery in Mr. Woolman's point about the higher lead at the bottom end. That is where we do get the higher lead, and we shall show on the prints of these ingots which have been sectioned—and it is common to almost all ingots—that one does get a row of lead spots round the end of the chilled crystals towards the bottom end of the ingot. The extent of that depends upon many factors. I would put the temperature of the steel first, but after that there is the size of the lead, which we control very carefully, and the method of adding it. The thought which Mr. Woolman voices as to whether the reduced ductility at high temperatures caused by lead is the real explanation of the improved machinability is a very interesting and, to me, a new one; I should like to thank him for it.

MERWINITE IN THE SYSTEM CaO-MgO-SiO₂.*

By T. W. PARKER, M.Sc., Ph.D., A.I.C., AND R. W. NURSE, M.Sc.
(BUILDING RESEARCH STATION, D.S.I.R., GARSTON, HERTS.).

SUMMARY.

Merwinite has been known for some time, as both a natural and an artificial mineral, but has not been detected as a stable phase in the system CaO-MgO-SiO₂. The present work establishes the primary phase field of merwinite in this system, and gives the position of the invariant points with the neighbouring fields of larnite, akermanite, monticellite and periclase. The pure mineral itself melts incongruently at 1590° C., forming 2CaO.SiO₂ and liquid.

The application of the data to problems of dolomite-silica refractories is discussed. It is shown that compositions of this type should be completely stable to both falling and hydration under all conditions of heating and cooling, when the CaO/SiO₂ ratio is less than 1.20, but that such mixtures form relatively large percentages of melt at fairly low temperatures and would therefore probably not be satisfactory refractories.

It is well known that falling blast-furnace slags can be stabilised by substituting MgO for part of the CaO in the slag composition, and, in practice, it appeared that stabilisation by this means covered a wider composition range than could be predicted on existing phase data. It is shown that the interposition of a merwinite primary field leads to deductions giving a greater agreement between theory and practice.

The data also provide confirmation of one point in Bowen's studies on the metamorphosis of siliceous limestone.

INTRODUCTION.

THE history of the discovery of merwinite, 3CaO.MgO.2SiO₂, both as a natural and as an artificial mineral, has been given by Phemister in a recent paper.⁽¹⁾ The increasing use of siliceous materials to stabilise dolomite refractories, and the use of a dolomitic flux for the stabilisation of blast-furnace slag, mean that a knowledge of the conditions under which merwinite may be formed is of some technical importance. As was pointed out in the discussion on Phemister's paper, it was apparent that merwinite was likely to have a primary phase field in the system CaO-MgO-SiO₂. The present investigation, which is concerned with a phase equilibrium study of the appropriate portion of this ternary system, shows this to be the case.

EXPERIMENTAL.

The methods used were similar to those commonly employed in the study of silicate and allied systems. Suitably prepared mixes of

* Received November 16, 1942.

known composition were heated to the required temperature and quenched, and, from microscopic examination of the products, the temperature of appearance of different phases was determined. From these data the primary phase fields, boundary curves and invariant points are derived.

The compositions were prepared from magnesium carbonate, crushed quartz and precipitated calcium carbonate. The analyses of these materials are given in Table I.

TABLE I.—*Analyses of Raw Materials.*

Analyses by F. McConnell, H. Andrews and H. Parker.

	MgO. %.	CaO. %.	SiO ₂ . %.	Al ₂ O ₃ . %.	Fe ₂ O ₃ . %.	(Na,K) ₂ O. %.	Loss on Ignition. %.
Magnesium oxide .	97.47	Nil	Trace	...	0.01	0.21	2.26
Quartz .	0.04	Nil	99.82	0.10	0.04	...	0.06
Calcium carbonate .	Trace	55.92	Trace	0.03	44.01

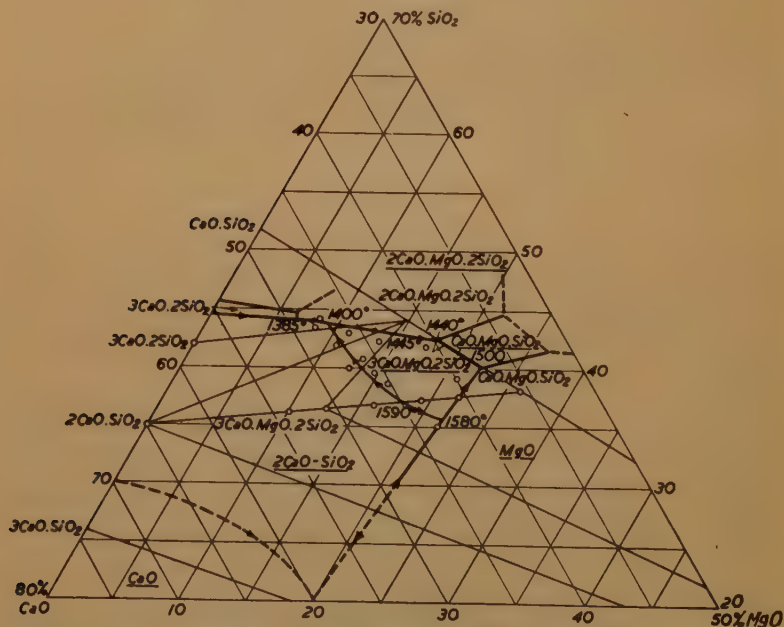
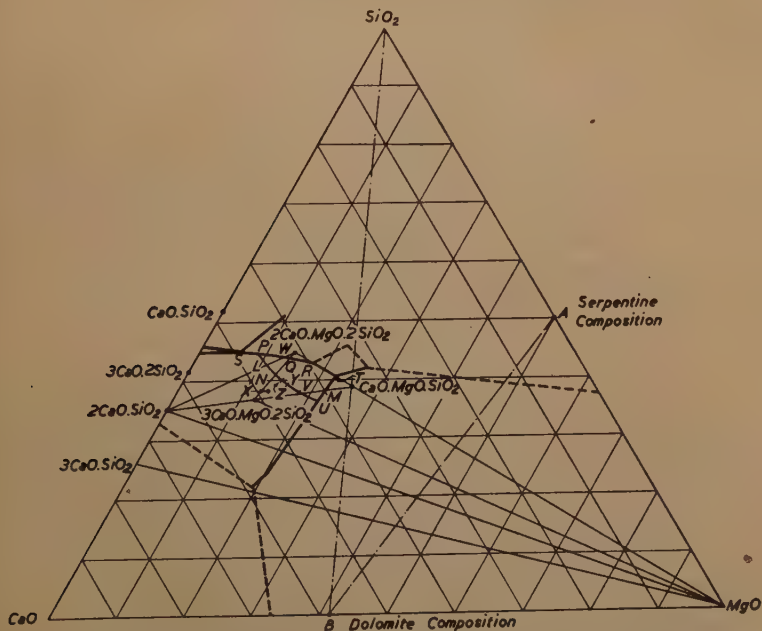


FIG. 1.—Field of Merwinite in the System CaO—MgO—SiO₂. Primary phases underlined; arrows indicate falling temperatures; experimental compositions marked by circles.

The dry materials were mixed together in the calculated proportions required for each desired composition and ground to pass a 180-mesh B.S. sieve and then heated at 1200° for 1 hr., followed by 1 hr. at a temperature sufficient to sinter the preparation. Small charges of about 0.1 g. were then heated in the small tube furnaces previously described⁽²⁾ and quenched in water and the products examined microscopically. The optical properties of the phases encountered are given in Table II. Fig. 1 shows the compositions investigated, and the boundary curves and direction of falling

TABLE II.—*Optical Properties of Primary Phases.*

Mineral Name.	Composition.	Refractory Indices.			
		N_g .	N_m .	N_p .	
Akermanite	C_2MS_2	1.639	...	1.633	Uniaxial positive, prismatic.
Monticellite	CMS	1.653	1.646	1.639	Negative, $2V = 90^\circ$.
Larnite	C_2S	1.737	1.720	1.715	Positive, $2V$ large.
...	C_2S from decomposition of C_4MS_2	<1.735	?	1.708	Nearly uniaxial.
Merwinite	C_3MS_4	1.724	1.711	1.708	Positive, $2V = 70^\circ$, polysynthetic twinning.

FIG. 2.—The Relationship of the Merwinite Field to the Complete System CaO-MgO-SiO_2 .

temperature in the part of the system investigated. Fig. 2 shows the relation of the merwinite field to the complete system $\text{CaO-SiO}_2\text{-MgO}$, and the composition regions involved in the discussion which follows on dolomite refractories (*see below*). Fig. 3(a) shows the temperature distribution along the boundary curve $\text{C}_2\text{S-C}_3\text{MS}_2$, and Fig. 3(b) that along the boundary curves $\text{C}_2\text{MS}_2\text{-C}_2\text{S}$ and $\text{C}_2\text{MS}_2\text{-C}_3\text{MS}_2$.* The quench data are given in Table III.

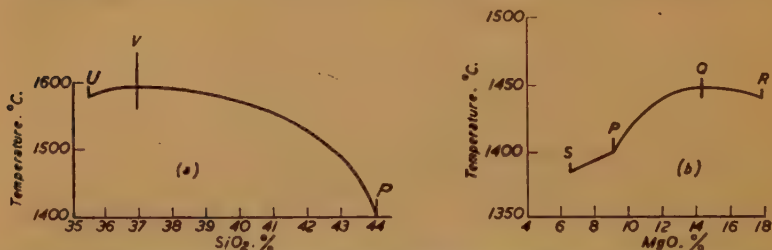


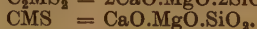
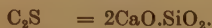
FIG. 3.—Temperatures on the Boundary Curves (a) $2\text{CaO.SiO}_2\text{-3CaO.MgO.2SiO}_2$, and (b) $2\text{CaO.MgO.2SiO}_2\text{-2CaO.SiO}_2$ and $2\text{CaO.MgO.2SiO}_2\text{-3CaO.MgO.2SiO}_2$.

The glasses obtained from compositions in the merwinite field were very liable to be strained, giving an anomalous birefringence when examined microscopically. Very large quench growths of olivine-like material of variable refractive index were also encountered; these disappeared as soon as a few definite primary crystals were formed. Merwinite was distinguished from C_2S by the lower refractive index and by the characteristic twinning bands. Compositions examined on the $\text{C}_2\text{S-C}_2\text{MS}_2\text{-CMS}$ line showed evidence of some solid solution of merwinite in C_2S over the portion of the line in which C_2S appeared as a primary phase, the refractive index of the latter phase being lowered and the axial angle becoming very small. There appears to be no solid solution of C_2S in merwinite, however. Phemister has noted that C_2S has a small axial angle in some blast-furnace slags.†

INVARIANT POINTS AND CRYSTALLISATION PATHS.

The existence of the C_3MS_2 field introduces two new invariant points into the system; point P (Fig. 2) is the invariant point $\text{C}_2\text{MS}_2\text{-C}_3\text{MS}_2\text{-C}_2\text{S}$ ($\text{CaO } 47.2\%$, SiO_2 43.6% , $\text{MgO } 9.2\%$) at 1400°C ., and point U the invariant point $\text{C}_3\text{MS}_2\text{-C}_2\text{S-MgO}$ ($\text{CaO } 42.6\%$,

* The short notation for silicate and similar compounds which has been adopted by workers in this field is used in the present account; *i.e.* :



Oxides such as CaO , MgO , SiO_2 are written in full.

† Private communication.

TABLE III.—*Quench Data.*

No.	Composition. %.			Results.
	CaO.	SiO_2 .	MgO.	
1	41.0	41.5	17.5	1470° C., glass. 1460° C., glass + merwinite. 1440° C., glass + merwinite + akermanite. 1430° C., merwinite + akermanite + monticellite.
2	40.0	39.5	20.5	1510° C., glass. 1500° C., glass + merwinite. 1490° C., glass + merwinite + MgO.
3	43.9	42.3	13.8	1500° C., glass. 1490° C., glass + merwinite. 1440° C., glass + merwinite + akermanite.
4	45.3	41.3	13.4	1480° C., glass. 1470° C., glass + merwinite. 1435° C., glass + merwinite + akermanite.
5	40.8	37.4	21.8	1600° C., glass. 1590° C., glass + a little MgO.
6	37.5	40.1	22.4	1500° C., glass + a little MgO. 1490° C., "eutectic" structure, some glass.
7	43.4	35.0	21.6	1650° C., MgO + 2CaO.SiO_2 . 1580° C., MgO + merwinite.
8	46.0	43.0	11.0	1470° C., glass. 1460° C., glass + a little merwinite. 1425° C., glass + merwinite + akermanite.
9	47.2	43.8	9.0	1400° C., very little merwinite + glass. 1390° C., merwinite + akermanite.
10	47.5	44.5	8.2	1400° C., glass. 1390° C., glass + akermanite. 1380° C., glass + akermanite + 2CaO.SiO_2 .
11	48.1	43.7	8.2	1430° C., trace 2CaO.SiO_2 + glass.
12	47.5	40.0	12.5	1580° C., glass. 1570° C., glass + 2CaO.SiO_2 . 1560° C., glass + 2CaO.SiO_2 + merwinite.
13	45.0	38.0	17.0	1590° C., glass. 1580° C., glass + 2CaO.SiO_2 . 1570° C., glass + 2CaO.SiO_2 + merwinite.
14	46.0	39.5	14.5	1580° C., glass. 1570° C., glass + merwinite.
15	47.3	41.6	11.1	1560° C., glass. 1550° C., glass + 2CaO.SiO_2 .
16	42.2	36.0	21.8	1590° C., glass. 1580° C., glass + MgO + merwinite.
17	43.5	37.2	19.3	1590° C., glass. 1580° C., glass + merwinite.
18	47.3	36.7	16.0	1650° C., 2CaO.SiO_2 + glass. 1590° C., merwinite + glass.
19	51.2	36.5	12.3	1650° C., glass + 2CaO.SiO_2 . 1590° C., merwinite.

SiO_2 35.5%, MgO 21.9%) at 1580°C .; neither is a eutectic. The invariant points C_3MS_2 -CMS-MgO and C_3MS_2 -CMS- C_2MS_2 were found to be coincident, within the experimental error, with the C_2S -CMS-MgO and C_2S -CMS- C_2MS_2 points respectively on Greig's⁽³⁾ modification of Ferguson and Merwin's⁽⁴⁾ diagram. On the boundary curve between C_3MS_2 and C_2MS_2 there is a temperature maximum (1445°C .) at the intersection of the line C_2MS_2 - C_3MS_2 (point Q, Fig. 2); this maximum would be difficult to distinguish experimentally from the maximum which Ferguson and Merwin quoted as existing at the intersection of the line C_2S - C_2MS_2 (point W). On the boundary between C_2S and C_3MS_2 a maximum occurs at the intersection of the projection of the line C_2S - C_3MS_2 (point V). This point gives the decomposition temperature of C_3MS_2 (1590°C .).

Crystallisation paths in the system can be determined by means of the established methods for the graphical determination of the order and quantity of the phases appearing with changing temperature. The shape and position of the primary phase fields in relation to the triangles delimiting the phases present on final crystallisation are such that the type of crystallisation path often introduces a "disappearing phase." A particular example is that of crystallisation paths of compositions in the triangle C_3MS_2 - C_2MS_2 -CMS, in which the final equilibrium results in the formation of the three crystalline phases C_3MS_2 , C_2MS_2 and CMS. Compositions in the area C_3MS_2 -N-V within this triangle first crystallise C_2S on cooling, this compound becoming a disappearing phase. The order and method of crystallising can be illustrated by considering the behaviour of the composition X, Fig. 2, which lies in this region, and which has a final melting point of about 1750°C .

As the melt is cooled below this temperature, crystallisation of C_2S will begin and the composition of the remaining melt will be given by the intersection of the line C_2S -X with the contour representing the temperature reached. At 1580°C . this intersection will be at Y on the C_2S - C_3MS_2 boundary. On further cooling, C_2S will redissolve while C_3MS_2 separates, the trace of the liquid composition being the boundary curve C_2S - C_3MS_2 .

The composition of the solid mixture of C_2S and C_3MS_2 will be represented by points on the line C_2S - C_3MS_2 and determined by the point of intersection of the C_2S - C_3MS_2 line with a line drawn through the composition of the liquid and the original composition X. At point Z, the line Z-X passes through C_3MS_2 ; all the C_2S will then have disappeared, only one solid phase, merwinite, remaining. An extra degree of freedom is thus gained, and the liquid composition will cross the merwinite field with falling temperature. The next phase change occurs when the line C_3MS_2 -X produced, representing the liquid composition, intersects the boundary curve C_3MS_2 - C_2MS_2 . At this point merwinite and akermanite crystallise together, and the liquid composition then follows the boundary curve in the direction

of falling temperature. The melt becomes solid at 1440°C ., when the liquid composition reaches point *R*. The final composition is thus merwinite, akermanite and monticellite.

The remainder of compositions in the $\text{C}_3\text{MS}_2\text{-C}_2\text{MS}_2\text{-CMS}$ triangle show straightforward crystallisation paths except in the small area CMS-T-M (Fig. 2). Within this area MgO is the primary phase and the order of crystallisation is MgO , then MgO and C_3MS_2 , until the invariant point *T* is reached. At point *T* the MgO redissolves and CMS crystallises, the solid phases being then C_3MS_2 and CMS . The residual liquid composition then passes along the boundary line TR with crystallisation of C_3MS_2 and CMS until point *R* is reached, when the composition solidifies completely with the formation of C_3MS_2 , CMS and C_2MS_2 .

Merwinite itself is a disappearing phase in the area PWL of the merwinite primary phase field. A small portion of this area near point *P* projects into the triangle $\text{C}_3\text{S}_2\text{-C}_2\text{MS}_2\text{-CS}$ (this may be most clearly seen by reference to the enlarged diagram of Fig. 1), and in this area both merwinite and C_2S occur as disappearing phases, the order of crystallisation being C_3MS_2 ; C_3MS_2 and C_2MS_2 ; C_2S and C_2MS_2 ; C_3S_2 and C_2MS_2 ; and C_3S_2 , C_2MS_2 and CS .

C_2S is also a disappearing phase in the system $\text{C}_3\text{MS}_2\text{-CMS-MgO}$, in compositions falling in the area limited by $\text{C}_3\text{MS}_2\text{-V-MgO}$. The significance of this is discussed later.

The equilibrium diagram can be applied to two industrial problems, namely those of the stabilisation of dolomite bricks for refractory purposes and the stabilisation of blast-furnace slag for use as an aggregate in concrete or as a roadstone. It also offers confirmation of some points in the theory of the metamorphosis of siliceous limestones. These applications are discussed in the following sections.

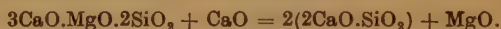
STABILISATION OF DOLOMITE REFRACTORIES.

Fired dolomite cannot be used as a refractory because the CaO formed, unlike the MgO , does not become so dead-burnt that hydration is effectively prevented. Consequently bricks made from burnt dolomite are attacked by atmospheric moisture when cool, with the formation of a fine powder of calcium hydroxide. The bricks may be stabilised sufficiently for practical use by the addition of sand or siliceous materials. In one form of this product the final composition desired is a mixture essentially of periclase and tricalcium silicate, the composition being adjusted so that a very small amount of C_2S is formed.⁽⁵⁾ In order to prevent the inversion of $\beta \text{C}_2\text{S}$ to $\gamma \text{C}_2\text{S}$ with its attendant large increase of volume, stabilising agents such as P_2O_5 , Cr_2O_3 or B_2O_3 are added in very small amounts. Even when "dusting" due to C_2S is prevented in this way, the bricks may become unstable in moist air at room temperature following

prolonged heating at temperatures below 1200°C. , on account of the formation of free CaO by the reaction :



Mixtures of silica and dolomite will lie on a line (Fig. 2) drawn between points SiO_2 and B , or to the high- CaO side of this line if the dolomite contains excess limestone. It can be deduced that, with increasing content of silica, the following mixtures are possible in that part of the system now investigated : CaO and MgO ; CaO , C_3S and MgO ; C_3S and MgO ; C_3S , C_2S and MgO ; C_2S and MgO ; C_2S , C_3MS_2 and MgO ; C_3MS_2 and MgO ; C_3MS_2 , CMS and MgO ; C_3MS_2 and CMS ; and CMS . Of these ten mixtures, the first six will be only partially stable, because of the possibility of forming either γ C_2S or free CaO . Various British and American patents referring to bricks composed of merwinite and magnesia are discussed in Phemister's paper.⁽¹⁾ When these bricks are used in circumstances permitting reaction with CaO , mineralisers must be added to prevent dusting of the C_2S formed by the reaction :



The bricks examined by Reinhart⁽⁶⁾ were apparently of the C_3MS_2 - CMS - MgO type.

Pure merwinite has been tested⁽⁷⁾ * as a refractory material, and proved to have poor slag resistance and low spalling resistance. A mixture of this kind contains very much more CaO than dolomite-silica mixtures, and it does not follow that refractories of the latter type which contain merwinite will not be satisfactory. In fact, a high slag resistance is claimed for the merwinite- MgO type of brick. One effect of choosing a mixture corresponding to pure merwinite would be that, in order to produce a liquid bond, the bricks would have to be fired above 1590°C. At this temperature, however, a large quantity of C_2S would be formed, and the bricks if rapidly cooled below 1590°C. would retain much of the C_2S in a metastable condition. On further cooling, the bricks would disintegrate, owing to the β - γ inversion. This was found to be the case by Chadeyron and Rees. The latter authors also investigated⁽⁸⁾ a mixture which was intended to be on the line C_2S - MgO , and was stabilised by the addition of borates, phosphates or chromates. When allowance is made for the CaO required to react with the R_2O_3 present as impurities, and in some cases for CaO required to react with the stabiliser, the mixtures actually fall inside the triangle C_3MS_2 - C_2S - MgO . The description given of thin sections of these mixtures⁽⁷⁾ (*loc. cit.*, p. 270) would indicate that merwinite was present. The refractory properties were said to be promising.

The mixtures of pure dolomite and silica (*i.e.*, on the line B - SiO_2 (Fig. 2)) which fall in the C_3MS_2 - CMS - MgO triangle can only form

* References to the *Bulletin of the British Refractories Research Association* are made by permission of the Director, Mr. A. T. Green.

C_2S under very limited conditions. Those mixtures in this triangle between the $\text{C}_3\text{MS}_2\text{-MgO}$ composition line and the line MgO-U (Fig. 2) will consist of MgO , merwinite and monticellite below 1500°C . Above this temperature MgO , merwinite and liquid are formed; at 1580°C . the merwinite is decomposed, forming C_2S ; and C_2S and MgO occur together until a temperature is reached at which MgO is the only solid phase. Compositions made from silica and a dolomitic limestone may fall in either of the triangles $\text{C}_3\text{MS}_2\text{-CMS-C}_2\text{MS}_3$ or $\text{C}_3\text{MS}_2\text{-CMS-MgO}$ in regions where C_2S can crystallise as a primary phase. For the latter system, C_2S will react to form merwinite at the invariant point U at 1580°C ., while in the former it will react at a point on the boundary curve $\text{C}_2\text{S-C}_3\text{MS}_2$ between points V (1590°C .) and N (1570°C .) in Fig. 2. Thus, all compositions within these triangles are stable unless cooling takes place from above 1570°C . sufficiently rapidly to prevent the C_2S from reacting as a disappearing phase.

Apart from questions of stability, the suitability of dolomite-silica mixtures for refractories will be determined by properties such as refractoriness-under-load and firing shrinkage, which will depend, at least partly, on the temperature of liquid formation and the amount of liquid formed. Table IV. gives the amounts of liquid formed at various temperatures for the principal types of mixture.

TABLE IV.—*Amounts of Liquid Formed at Various Temperatures in Dolomite-Silica Mixtures.*

Composition of Dolomite-Silica Mixture.	SiO_2 , %.	Liquid, %, Formed at—			
		1600°C .	1550°C .	1500°C .	$<1500^\circ \text{C}$.
Monticellite	33.2	100	98	95	Nil
Intersection with the line MgO U	33.5	93	60	47	Nil
Intersection with the line $\text{MgO-C}_3\text{MS}_2$	29.3	60	Nil	Nil	Nil
Mixture examined by Chadeyron and Rees (86% dolomite, 14% sand)	25.0	28	Nil	Nil	Nil

It is seen from Table IV. that an increase in SiO_2 beyond 29.3% (the value corresponding to the intersection with the $\text{MgO-C}_3\text{MS}_2$ line) results in liquid formation at a lower temperature and a large increase in the amount of liquid present at any temperature. Chadeyron and Rees found the limiting mixture of dolomite and sand to be 83% of dolomite and 17% of sand. The calculated SiO_2 content for this mixture after firing is 30.4%, which is in good agreement with the value 29.3% deduced above.

When serpentine is used for stabilising, the resultant mixtures will lie on line AB (Fig. 2) or in the triangle $A\text{-}B\text{-}\text{SiO}_2$. The fore-

going deductions may also be applied to such mixtures, except that even with dolomitic limestone instead of dolomite it would not be possible to obtain C_2S as a primary phase. For these mixtures the liquid contents in Table IV. will be considerably reduced, although the temperatures of liquid formation are unchanged.

To sum up, it is possible from the phase data to select mixtures of dolomite and siliceous material which will be completely stable both to falling and to hydration under all conditions of heating and cooling (*i.e.*, compositions having a CaO/SiO_2 ratio of less than 1.20). The mixtures, however, form relatively large percentages of liquid rapidly at fairly low temperatures, and therefore would probably not be satisfactory refractories. The phase data also show that it is possible for Chadeyron and Rees' limiting mix (83% of dolomite, 17% of sand) to be free from any falling troubles if the temperature of the mixture in use does not exceed $1600^\circ C.$, but that it is theoretically possible for the mixture to disintegrate if it is cooled rapidly from temperatures above $1600^\circ C.$

Mixtures in the $C_2S-C_3MS_2-MgO$ triangle, said to be suitable in certain positions in open-hearth and other furnaces, must, from the phase data, always contain C_2S , and must therefore require stabilising with mineralisers.

STABILISATION OF BLAST-FURNACE SLAG.

Merwinite as a constituent of blast-furnace slags has recently been described by Phemister,⁽¹⁾ and Parker and Ryder⁽⁹⁾ refer to the possible influence of the compound in preventing slags high in magnesia from falling on cooling. Partial substitution of dolomite or magnesian limestone for limestone in the blast-furnace burden is one of the recognised methods of stabilising slags against falling, in order to make them suitable as concrete aggregates or road stones. The cause of falling is the presence of crystalline C_2S in the slag, the β - γ inversion of this compound causing disintegration of the solid mass. Blast-furnace slag compositions which do not contain C_2S in their final solid state do not fall and Parker and Ryder were able to show that some extension of non-falling compositions by substitution of MgO for CaO could be predicted on the basis of existing phase data, but that, in practice, stabilisation was carried to compositions beyond the limit predictable by the existing phase data. The most obvious explanation of the discrepancy was the interposition of a merwinite primary phase field in place of C_2S in the crystallisation paths of the compositions involved.

The present data confirm this. The system $CaO-MgO-SiO_2$ is a bounding system of the quaternary system $CaO-MgO-SiO_2-Al_2O_3$ to which blast-furnace slags belong essentially, and, although slags never fall entirely in the $CaO-MgO-SiO_2$ system (*i.e.*, they always

contain Al_2O_3), it is possible to use deductions from the CaO-MgO-SiO_2 system to indicate the course of crystallisation which may occur.

Parker and Ryder showed that (excluding sulphur present as CaS) the probable plane of demarcation of falling from non-falling slags of the higher MgO contents in the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$ system was represented by an equation :

$$\text{CaO} = 0.93 \text{ SiO}_2 + 0.55 \text{ Al}_2\text{O}_3.$$

This equation is that of a plane passing through the points MgO , C_2MS_2 and C_2AS . The plane cuts the CaO-MgO-SiO_2 system in a line from MgO to C_2MS_2 and is in fact a line of ternary compositions completely identified in that the ratio of CaO to SiO_2 is 0.93. It applies, however, only to compositions having contents of MgO of 15% or more (15% being the MgO content of C_2MS_2); at lower contents it is necessary to adopt a different plane, *i.e.*, that which intersects the CaO-MgO-SiO_2 system in the line from C_2MS_2 to the $\text{C}_3\text{S}_2\text{-CS}$ binary eutectic.

If blast-furnace slags contained only CaO , MgO and SiO_2 it would be predicted that no falling phenomenon would be shown by any composition lying on the SiO_2 side of a line running from the $\text{C}_2\text{S-C}_3\text{S}_2$ invariant point to S , P , along the $\text{C}_2\text{S-C}_3\text{MS}_2$ boundary to U , and then from U to MgO , because in that area C_2S never appears as a crystalline phase. This represents an extension of the stable area previously predicted by Parker and Ryder, which was an area on the SiO_2 side of a line from the $\text{C}_3\text{S}_2\text{-CS}$ eutectic to C_2MS_2 and from C_2MS_2 to MgO .

It is not possible to suggest any accurate amendment of the existing equation, however, until further data are obtained of the position of the merwinite field in the quaternary system $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$. The present data simply give additional verification of Parker and Ryder's assumption that their equation is on the safe side of non-falling compositions. The number of slags affected by this too conservative choice of plane is not large in practice.

METAMORPHISM OF SILICEOUS LIMESTONE.

Bowen⁽¹⁰⁾ has discussed the progressive metamorphism of siliceous limestones and dolomites, and has shown that the mineral combinations present are an indication of the maximum temperature reached. In this connection, he deduces that merwinite should not co-exist with wollastonite. He also states that larnite (2CaO.SiO_2) and merwinite can co-exist and that the decomposition :



is probable. The delineation of a primary phase field of merwinite confirms these deductions of Bowen's, and also introduces a higher point in the suggested temperature scale, *i.e.*, the decomposition of merwinite at 1590°C .

ACKNOWLEDGMENT.

The work was carried out at the Building Research Station of the Department of Scientific and Industrial Research, and the paper is published by permission of the Director of Building Research.

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CORRESPONDENCE.

Mr. R. B. SOSMAN and Mr. R. B. SNOW (Research Laboratory, United States Steel Corporation, Kearny, New Jersey, U.S.A.) wrote : We have been interested in comparing the authors' equilibrium diagrams (Figs. 1 and 2) with the results obtained by E. F. Osborn and J. F. Schairer at the Geophysical Laboratory in 1938-42 and presented in part by Osborn before the American Ceramic Society, April 22, 1942, but unfortunately not yet in print because the investigators have been occupied with emergency work.¹ Having had the use of the results since their public presentation, and having made some investigations of our own in this system, we are authorised by Dr. Osborn to present this brief discussion.

Fig. A is redrawn from two of Osborn's diagrams, with Parker and Nurse's lettering added from Fig. 2. The temperatures, given in Fig. A on the International Scale, are in fairly good agreement with those of Parker and Nurse. The most important difference between the diagrams is in the composition of the invariant point *U*, a difference which considerably influences the course of crystallisation. Parker and Nurse have it at CaO 42.6%, MgO 21.9%, SiO₂ 35.5%, which brings it within the composition triangle C₃MS₂-CMS-MgO. The more probable composition is Osborn's, CaO 43.0%, MgO 18.2%, SiO₂ 38.8%, bringing it within the triangle C₃MS₂-CMS-C₂MS₂ and eliminating the maximum marked *V* in the boundary curve *U-P*, see Figs. 1 and 3(a).

¹ Published, since this contribution was submitted, in *Journal of the American Ceramic Society*, 1943, vol. 26, No. 10, p. 321.

Parker and Nurse also have the invariant point P relatively much higher in MgO and lower in CaO than Osborn, although the SiO_2 percentage is identical. This difference does not, however, affect the course of crystallisation.

There is not space here for a detailed discussion of the crystallisation phenomena, which are given fully in Osborn's paper as submitted to the *Journal of the American Ceramic Society*.

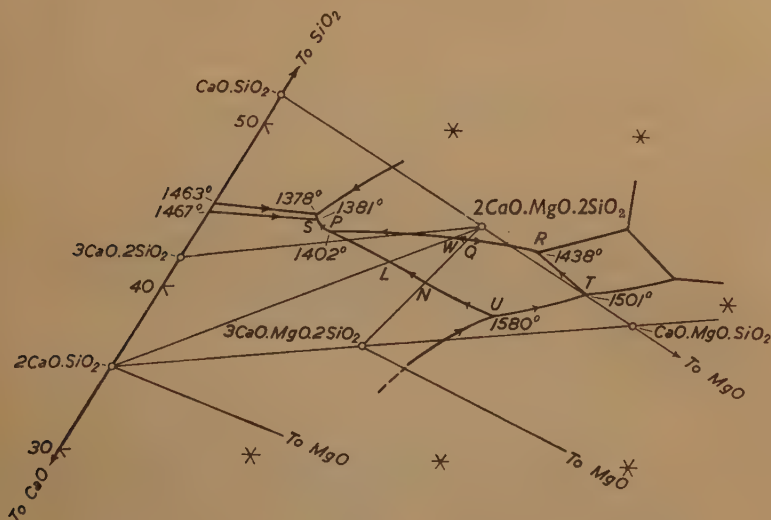


FIG. A.—Equilibrium Diagram of Part of the System CaO-MgO-SiO_2 including the field of merwinite. Data of E. F. Osborn. (Temperatures on the International Scale.)

We may add that another important application of the data, besides those discussed by Parker and Nurse, is found in the so-called magnesite bottom of the open-hearth steel furnace, where, on account of the presence of lime-bearing open-hearth slag and the frequent use of clinkered dolomite, merwinite is always a possible phase.

AUTHORS' REPLY.

The AUTHORS replied: We were not aware that work on an identical part of the CaO-MgO-SiO_2 system was in progress at the Geophysical Laboratory, apparently during much the same period

in which our own work was being carried out, and we wish to thank Mr. Sosman and Mr. Snow for drawing attention to it.

The agreement on temperatures is within the experimental error of our determinations. The difference in the composition of the invariant point *U* is, however, considerable, and, as mentioned by Sosman and Snow, affects the courses of crystallisation in this area of the system. It has been noted in the main text that there is considerable difficulty in quenching liquids to glasses in this part of the system. Crystal growths of an olivine-like character appear, but, once a few crystals of a stable phase occur, these olivine-like growths tend to disappear and the charges contain stable phase and glass. This criterion was largely used in deciding on the primary phase. In some cases it was observed that small crystals of MgO were present with the olivine-like growths, but it was considered that these either might have formed with the olivine-like material or, when present in traces only, might represent incomplete reaction of the starting product—it is difficult to free compositions from the last traces of MgO. Fig. 1 will show that we have not examined many composition points in the area concerned, but our mix 17 (Table III.) is a characteristic case. On Osborn and Schairer's diagram our mix 17 should have MgO as the primary phase. In other words, the presence of MgO above 1580° C. in this mix should be attributed to this compound being a primary phase rather than occurring through inability to quench to a true glass or to residual unreacted MgO.

Since receiving Sosman and Snow's comments we have made some further tests in an attempt to resolve this point. Unfortunately, circumstances have not permitted any very elaborate additional investigation, but the following gives some additional data. A small charge of mix 17 was heated on iridium foil by means of an oxy-gas flame to apparent fusion and quenched. Examination of the product showed no MgO crystals in it. The product was then used for quenching experiments in the quench furnace. At 1590° C. MgO crystals again appeared with the olivine material. This disposes of the possibility that the MgO may be residual material through incomplete reaction and, while not completely conclusive, is a strong pointer in the direction that it is the primary phase.

Another method has also been tried. According to our diagram, pure merwinite should decompose to $2\text{CaO} \cdot \text{SiO}_2$ and liquid at 1590° C. According to Osborn and Schairer's diagram the first decomposition of merwinite should occur at 1580° C. A heating curve has now been carried out by Mr. J. F. Ryder, of the Building Research Station, on a sample of merwinite which under the microscope contained only small traces of unreacted MgO. The curve shows a large thermal arrest at 1578° C. In view of these two new items, therefore, we accept the Osborn and Schairer placing of point *U*.

THE SOLIDIFICATION AND COOLING OF STEEL INGOTS.¹

NOTES ON AN EXAMINATION OF THREE TYPICAL INGOTS.

By E. F. LAW, A.R.S.M., AND VERNON HARBORD, A.R.S.M.
(MESSRS. RILEY, HARBORD AND LAW, LONDON).

(Figs. 1 to 49 = Plates XXX. to XXXVIII.)

*Paper No. 21/1943 of the Committee on the Heterogeneity of Steel
Ingots.*

SUMMARY.

A detailed microscopical investigation has been made of two ingots, Nos. 36 and 59, and a partial investigation of a third ingot, No. 65, previously studied by the Ingot Committee (*see* Fourth and Sixth Reports on the Heterogeneity of Steel Ingots, *Iron and Steel Institute, Special Reports No. 2* (1932) and *No. 9* (1935)). A careful study was made of the distribution of the phosphorus in relation to the carbon and sulphur, and a suggested explanation has been advanced to cover the mechanism of the freezing and subsequent cooling changes in the killed ingot.

Certain definite observations are recorded on the structure of ingot 59, and the existence of an intercrystalline material, believed to be a carbon-phosphorus complex, has been established in both ingots 59 and 65. This material predominates in the rim portion of ingot 59, but the authors have been unable to account for its formation and are uncertain as to whether it is a result of the rimming action or not. This point can be settled only by the examination of an ingot of similar composition but of non-rimming type.

Observations on the behaviour and type of sulphide distribution in all three ingots have been made and recorded, as well as on such variations in sulphides as occur between the rim and core in ingots 59 and 65.

The authors explain the incompleteness of their investigation, but consider that the detailed observations which they have made are of sufficient interest to warrant publication in view of the uncertainty as to when further work can be carried out towards its completion.

INTRODUCTION. •

SOME years ago the Ingot Committee suggested to one of the authors (E.F.L.) that an investigation into the formation and distribution of sulphides in steel ingots would be of value and

¹ Received February 26, 1943. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

offered to supply him with sections of typical ingots which had been prepared for and examined by the Committee.

As a preliminary step it was decided to make a detailed examination of sections of a killed medium-carbon steel (No. 36) and a low-carbon rimmed steel (No. 59). Full details of the history of these ingots are recorded in the Committee's Fourth Report on the Heterogeneity of Steel Ingots.¹

A very large number of chemical analyses was made in order to establish the degree of segregation, not only of sulphur but also of carbon, phosphorus and manganese, from the outside to the centre of the ingots, and special attention was given to the apparently anomalous behaviour of manganese in relation to sulphur segregation. Similar work has been carried out by others, and as the facts are now generally accepted the work need not be dealt with here. The information obtained from this investigation did not throw much light on the changes taking place during the solidification of an ingot, but it did serve to demonstrate that sulphur could not be considered by itself alone but in conjunction with carbon and phosphorus, and, further, that methods much more accurate than chemical analysis were essential. It was therefore decided to make a detailed microscopical examination of the two ingots, to which a third, ingot-iron, ingot (No. 65)² was later added, and several observations have been made and recorded which, it is hoped, will be of interest and may not only serve to add to such knowledge as has so far been obtained on the mechanism of ingot solidification and subsequent changes during cooling but may lead to further investigations into this interesting subject.

Even before the war it was not possible to pursue the investigation continuously, owing to the intervention of other work, and consequently it had to be laid aside for varying periods. After the outbreak of war it was not possible to proceed further except for a short period during the last six months. In view of the present uncertainties in carrying on such work, the authors feel that, though they fully realise the incompleteness of this investigation, it is better to put forward the results already obtained.

KILLED-STEEL INGOT No. 36.

The first ingot examined was No. 36 of the Ingot Committee's Fourth Report, being a medium-carbon killed ingot of the following composition :

Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0.400%	0.210%	0.054%	0.016%	0.820%

A slice from the outer wall to the ingot centre was obtained, a section of which was macro-etched and sulphur-printed (Figs. 1

¹ *Iron and Steel Institute, 1932, Special Report No. 2.*

² *Sixth Report on the Heterogeneity of Steel Ingots, Iron and Steel Institute, 1935, Special Report No. 9.*

and 2) before being cut up into eleven sub-sections for micro-examination, No. 1 being on the outside and No. 11 the centre of the ingot.

Observations on the General Appearance of the Structure.

Preliminary investigation of the series of sections through the ingot revealed the following characteristics :

(1) On the outside of the ingot in the chilled zone the boundaries of the pearlite grains were more angular, and there was little tendency for the inclusions, which were small and spherical, to group themselves together. Well-defined channels of ferrite were not present, and the ferrite appeared to be more broken up with pearlite than in the more slowly cooled specimens. Fig. 3 shows the general structure near the outside of the ingot, and Fig. 4 the more or less ragged boundaries of the pearlite grains.

(2) As the sections further into the ingot were progressively examined the pearlite grains became larger and more rounded; broad ferritic bands surrounded these grains, in the centre of which and at the junction of two or three such bands there was a marked tendency for grouping of sulphide particles and other inclusions. The early stage of development of these bands is shown in Fig. 5, and the final stage in Fig. 6. For want of a better term these bands were always spoken of as "channels" and will be referred to as such in these notes. The inclusions were larger and more elongated, and at times specimens of almost perfect crystals of manganese sulphide were found (Figs. 7 and 8). These inclusions were not situated along crystal boundaries, but their position was generally located by the channels of ferrite and frequently ran across crystal boundaries (Fig. 9). Occasionally in the more rapidly cooled part of the ingot near the outside inclusions were partially or entirely trapped in pearlite grains (Fig. 10).

(3) Sulphide particles generally were homogeneous in character, and after the midway point from outside to centre was reached they became less numerous in the channels.

(4) The general conditions outlined in paragraph 2 continued until the centre was reached, which was characterised by a mixture of large rounded grains of pearlite and a more broken-up structure, similar to the outside section (Fig. 11).

(5) Individual sulphide grains embedded in pearlite were frequently surrounded by a circular ring of free ferrite, especially in the more rapidly cooled parts near the outside of the ingot (Fig. 12).

Careful examination of the ingot structure from outside to centre suggested that in the more slowly cooled part of the ingot, where cooling was undisturbed, that portion of the steel which in

the solid ingot appears as pearlite was the first metal to freeze, ejecting the liquor rich in impurities, *viz.*, carbon, phosphorus, &c., together with entrained non-metallic inclusions, into the ferrite channels to form the filling-up of the skeletons of large dendrites. The middle of these channels, being highest in impurities, would freeze last and carry with it the greatest amount of dissolved impurities and inclusions.

Typical sections were therefore etched with Stead's reagent and also by electrolytic etching with caustic soda, and both these methods clearly showed absence of phosphorus in the ferrite lamellæ of the pearlite as well as in all the ferrite surrounded by or embedded in pearlite; the presence of phosphorus was shown in the ferrite channels in contact with pearlite grains, increasing towards the middle of the channels. This is apparent in Figs. 13, 14 and 15, which show the same field etched with nitric acid and for various periods of time by electrolytic soda attack.

This showed definitely that the metal which froze first and which finally became pearlite was free from phosphorus, this element being held in solution by mother-liquor freezing out at progressively falling temperatures as the phosphorus concentration increased.

In view of the fact that the pearlite areas were originally the liquid of the highest melting point, it seemed unlikely that at the moment of freezing they contained any impurity capable of lowering its melting point; it is more likely that it originally froze out as ferrite (*i.e.*, iron containing some manganese and silicon in solution) and that the carbon migrated from the iron-carbon-phosphorus mother-liquor in the channels after solidification. It seemed probable that after solidification and during cooling, the iron-carbon-phosphorus liquor broke down and that the carbon was divorced from the phosphoric areas and entered into the phosphorus-free ferrite, thus forming the pearlite as it exists when cooled.

Examination of a rimmed ingot (No. 59, *see* below) was being made at the same time, and certain observations of the structure supported the probability that, although in all likelihood the original freezing of a carbon-phosphorus-iron solution occurred, there was at a later stage in cooling a strong tendency for the carbon to be pushed away as far as possible from the phosphoric areas.

A piece of the killed ingot was therefore taken from a position rather nearer the centre than the outside and cut into four pieces; one was kept untreated for comparison. One piece was heated above Ar_3 and air-cooled. This showed that the pearlite had migrated into the ferrite channels, being broken up into smaller grains, but under low power it was still possible to locate the position of the channels. Sulphide particles remained unchanged in their original channel positions.

In all these experiments it was unfortunately impossible to photograph the same field in each case, as the specimen had to be re-

polished after treatment, but Figs. 16 and 17 show typical channels, while Figs. 18 and 19 illustrate a similar channel etched with nitric acid and picrate, respectively, after heating and air-cooling. The roughly triangular formation of the inclusions gives an indication of the shape and width of the original channel into which the carbon has migrated. A second piece was heated to the same temperature and quenched in water. A general martensitic structure was obtained, although the channels were clearly visible under relief polish, with sulphide inclusions in their original positions. Examination revealed hard martensite areas surrounded by the channels, greatly reduced in size, in which appeared to be a certain amount of dissolved carbon incapable of resolution, as these channels were faintly darkened by boiling alkaline sodium picrate. Fig. 20 depicts the section etched with nitric acid, and Fig. 21, etched with picrate, shows that the carbon migration has not been complete. A third piece from the same section was heated to above Ar_3 and air-cooled, reheated to the same temperature and very slowly cooled in the furnace. This resulted in migration of the carbon away from the channels, leaving them with their strings of sulphide particles unchanged; the pearlite did not completely agglomerate into the large original grains, but was more broken up; to a large extent, however, the original ingot structure was restored, as is shown in Figs. 22 and 23, etched, respectively, in nitric acid and alkaline sodium picrate.

These experiments showed clearly the ability of the carbide to migrate at this temperature, and also that at a temperature above Ar_3 it was still retained in the channels; the fact that when very slowly cooled from this temperature the movement from the channels was greatest is strong evidence that the higher-phosphoric areas tend to drive the carbide as far away as possible. The reason for the incompatibility of carbide and phosphide is open to discussion, but there appears to be no doubt about its existence, and the fact that carbon is readily able to diffuse in solid iron, whereas phosphorus is not, enables the separation to take place.

It is therefore suggested that in the normal cooling of a killed ingot the process of freezing and cooling operates on the following principles: Primary crystals of ferrite (containing some of the manganese and silicon, and possibly some carbon in solution but not the greater portion) entirely free from phosphorus are the first to crystallise as a homogeneous solid solution; the mother-liquor carrying the bulk of the carbon and all the phosphorus freezes progressively around these dendritic skeletons, giving the maximum carbon-phosphorus concentration in the centre of the channels so formed, in which are also collected the bulk of the sulphide and other inclusions. When the temperature falls below the Ar_3 point, the iron-carbon-phosphorus solution breaks down and the phosphide solution ejects the carbon, which is driven as far as possible away from the high-phosphorus areas (the distance

depending on the rate of cooling) and enters into the ferrite crystals which were the first to freeze, thereby converting them into pearlite areas found in the cooled ingot. The space originally occupied by the ferrite solid solution will vary according to the carbon and phosphorus contents of the steel. When the final migration of carbon in the solid state occurs there may be insufficient carbon to convert completely the whole to pearlite, so that some free ferrite may be found embedded in the final pearlitic areas usually in acicular form. The fact that such ferrite is found to be free from phosphorus is thus accounted for.

When the decomposition of the iron-carbon-phosphorus mother-liquor and the migration of the carbon in the solid state is accepted, it is seen that the freezing of a killed ingot proceeds in accordance with theoretical considerations and the views held by the late Dr. J. E. Stead. Moreover, it confirms the existence of the "iron-carbon-phosphorus complex" observed by Professor Andrew.¹

RIMMED-STEEL INGOT No. 59.

Following the examination of the killed ingot, a similar section from outside to centre of a rimmed ingot, No. 59, was obtained, and after macro-etching and sulphur-printing (Figs. 24 and 25) it was cut up into 22 micro-sections for detailed examination, No. 1 being on the outside wall of the ingot. The ingot had the following pit-sample analysis :

Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0.050%	Trace	0.027%	0.077%	0.470%

The rim of the ingot extended up to piece No. 10, the inner part of this section being more or less the transition stage from the rimmed to the unrimmed part of the ingot.

Broadly speaking, the essential differences between the rim and interior of the ingot were :

- (1) In the carbide and pearlite formation.
- (2) In the sulphide formation.

(1) In the rim the carbide appeared in most cases as an inter-crystalline material surrounding ferrite crystals; at times it became fairly massive, especially towards the inside of the rim. Pearlite, where it occurred, was in almost all cases surrounded by an envelope of carbide, which extended as strings penetrating along the crystal boundaries of surrounding ferrite (Figs. 26 and 27). On crossing the rim boundary these strings and envelopes ceased abruptly, normal pearlite being almost exclusively present for some distance into the core; from there onwards there was a reappearance of some envelopes and carbide strings, although normal pearlite predominated.

¹ Andrew and Howat, *Journal of the Royal Technical College, Glasgow*, 1932, vol. 2, Jan., p. 608.

In the foregoing paragraph the term "carbide" has been used to describe the envelopes and intercrystalline material, but further investigation, which will be described later, gave rise to serious doubt as to whether this constituent was free cementite.

(2) Sulphide particles, which were very small and scattered in the outside of the rim, increasing in size as slower cooling took place, were all of a complex type, the normal dove-grey constituent being comparatively rare. After crossing the rim boundary normal sulphide was predominant, although some complex sulphide particles were present (Fig. 28) and became more numerous towards the centre of the ingot.

The "Carbide" Material.

This constituent, which, as already mentioned, existed as envelopes and intercrystalline strings, was the subject of a great deal of investigation, as it did not appear to behave in all respects as normal cementite.

(1) It did not appear to be sufficiently hard; it was liable to "flow" slightly under polish (Fig. 29) and required careful polishing to obtain reliable surfaces for micro-examination.

(2) When etched with boiling alkaline sodium picrate solution these areas blackened very quickly, far more so than the cementite lamellæ in pearlite areas. It was possible to blacken this constituent completely before any staining of the pearlite cementite occurred, which was only shown up by further boiling in the solution. Fig. 30 shows the thick envelopes and strings in the rim and Fig. 31 the thinner envelopes in the core; Fig. 32 is typical of the centre of the ingot.

Since it is known that phosphoric areas are blackened by sodium picrate in a similar manner to cementite, it seemed possible that this constituent might be a phosphide-carbide material, and not pure cementite.

Compared with the killed ingot previously examined, and assuming, as seemed probable, that ferrite froze out first, leaving a solid solution containing carbon, phosphorus and iron, this solution would have a far greater concentration of phosphorus compared with carbon in this ingot, on account of its higher phosphorus and lower carbon contents. It seemed possible, therefore, that as complete a separation of the carbon and phosphorus after solidification as occurred in the killed ingot might not take place here, and that some entanglement of phosphide and carbide might be found round crystal boundaries.

Accordingly, a large amount of experimental work was carried out to try to obtain an etching reagent which would differentiate between cementite and phosphide solutions. No satisfactory reagent was actually found, though certain work did yield some evidence

to support the suggestion that the constituent was not true cementite.

One of the most encouraging methods depended on careful heat-tinting. It must be appreciated that the small amounts of the constituent present necessitated examination under high-power oil-immersion objectives, and it was extremely difficult to obtain good reliable fields properly tinted. Successfully heat-tinted specimens showed a different colour in strings and envelopes from that of the carbide lamellæ; some colour micrographs taken showed these differences. Whilst this evidence was not regarded as conclusive, it was sufficient to add some confirmation to the suggestion that the strings were not pure cementite.

In an attempt to obtain further evidence, piece No. 10, *i.e.*, the inner edge of the rim, in which envelopes and strings were most fully developed, was heated to 850°C . and very slowly cooled. The effect of this was to break up the pearlite into smaller areas and to reduce greatly the width of the strings and envelopes. Similar results were obtained on piece No. 4 in the rim, which was heated to 1000°C ., quenched in water, and annealed at 850°C . This reduction in width of the strings and envelopes, illustrated in general in Figs. 33 (untreated) and 34 (treated), might be explained by absorption or divorce of one constituent of the strings as a result of heating and slow cooling. Fig. 35 shows the effect of the annealing on a typical string (etched with nitric acid), and Fig. 36 a similar field etched with alkaline sodium picrate.

Apart from the two main differences between the rim and core already referred to, a less striking difference was observed, namely, that, whereas in the rim pearlite was angular and less frequent and sulphides were scattered haphazard, in the core pearlite more rounded in character and in greater quantity was found; this occurred in the part in which both the carbon and phosphorus contents were higher. Also there was a distinct tendency in this part of the core for grouping of inclusions similar to those found in the channels of the killed ingot. Figs. 37 and 38 show these characteristics in the rim and core, respectively.

To investigate this similarity between parts of the core and the killed ingot No. 36, specimens were etched by the electrolytic soda method, which failed to show any phosphorus concentration in the rimmed portion of the ingot similar to that found in the killed ingot. In the interior of the ingot beyond the rim there was definite evidence of phosphorus concentration and channelling as found in the killed ingot. Figs. 39 and 40 show the same field in a section of the core, etched, respectively, in nitric acid and by the electrolytic soda method.

Although the investigation was far from complete, it is suggested that in a rimmed ingot the freezing of the rim and of the interior is entirely different.

In the rim there seems to be no concentration of phosphorus

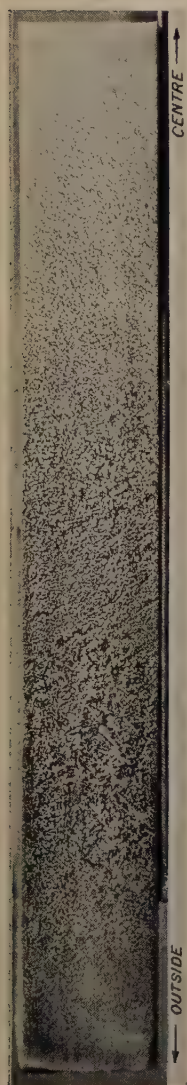


FIG. 1.—Macro-Etch of Slice of Ingot from outside to centre.



FIG. 2.—Sulphur Print of Slice of Ingot from outside to centre.



FIG. 3.—General Structure near Outside of Ingot. Etched with nitric acid. $\times 100$.

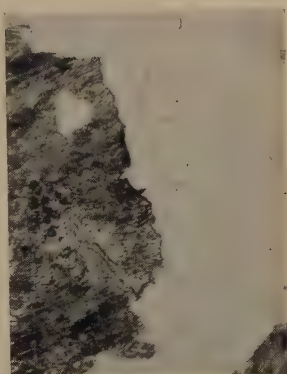


FIG. 4.—Same as Fig. 3; ragged boundaries of the pearlite grains. Etched with nitric acid. $\times 1000$.



FIG. 5.—Structure beyond the Chill; early stage of development of ferrite bands. Etched with nitric acid. $\times 100$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.
To face p. 496 p.]

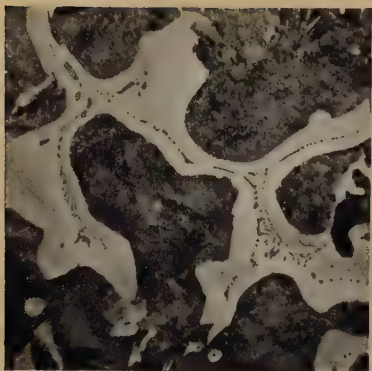


FIG. 6.—Midway to Centre of Ingot; maximum development of ferrite bands. Etched with nitric acid. $\times 100$.



FIG. 7.—Almost Perfect Crystals of Manganese Sulphide. Etched with nitric acid. $\times 1000$.

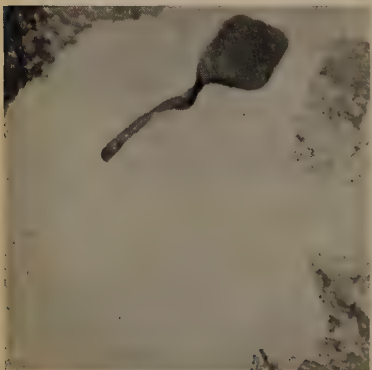


FIG. 8.—Another Example of Crystalline Form of Manganese Sulphide. Etched with nitric acid. $\times 1000$.

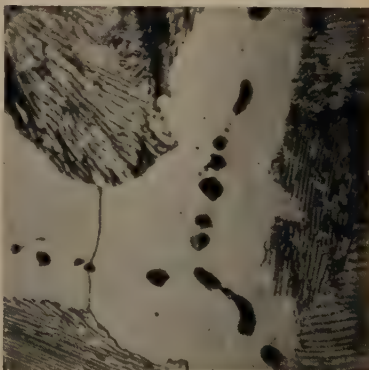


FIG. 9.—Manganese Sulphide Particles in Ferrite Channels crossing Crystal Boundaries. Etched with nitric acid. $\times 1000$.

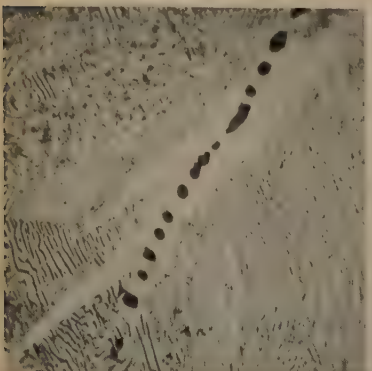


FIG. 10.—String of Inclusions partially trapped in Pearlite Grains near Outside of Ingot. Etched with nitric acid. $\times 1000$.

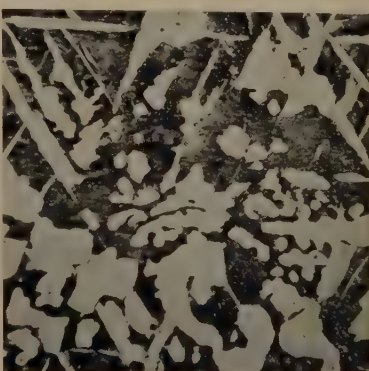


FIG. 11.—General Structure near Centre of Ingot. Etched with nitric acid. $\times 100$.

(Micrographs reduced to two-thirds linear in reproduction.)

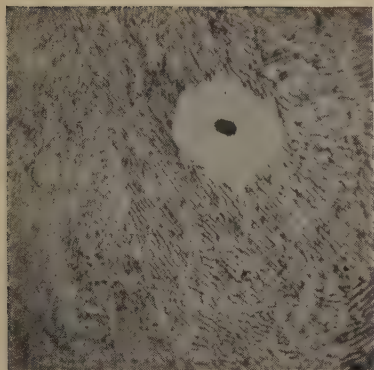


FIG. 12.—Sulphide Particles surrounded by Ferrite trapped in Pearlite Grains. Etched with nitric acid. $\times 1000$.

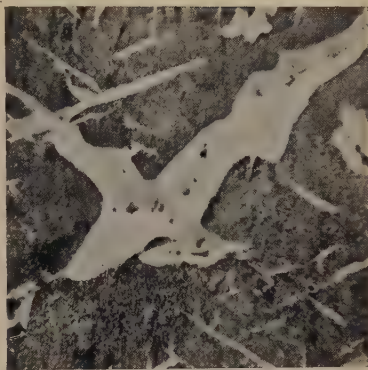


FIG. 13.—Typical Section near Centre of Ingot. Etched with nitric acid. $\times 100$.

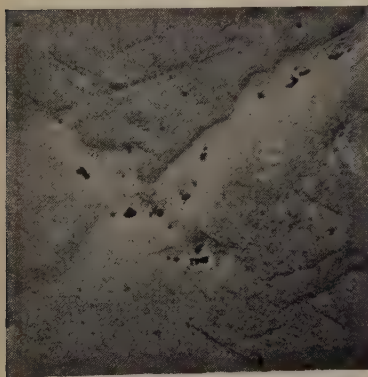


FIG. 14.—Same Field as Fig. 13, lightly etched by electrolytic soda attack. $\times 100$.

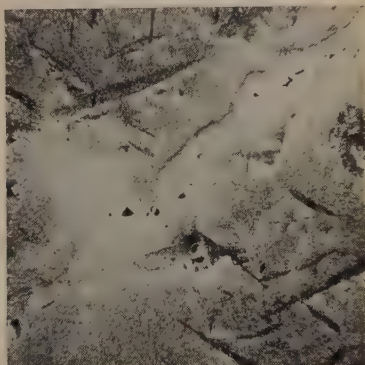


FIG. 15.—Same Field as Fig. 13, more deeply etched by electrolytic soda attack. Phosphoric ferrite in channel undarkened; phosphorus-free ferrite in pearlite darkened. $\times 100$.

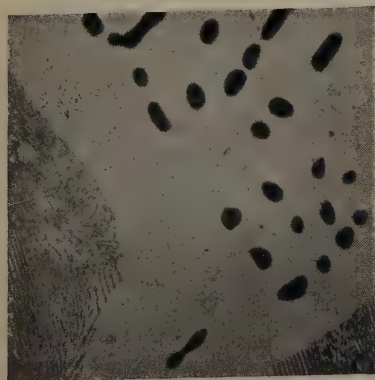


FIG. 16.—Typical Ferrite Channel with Manganese Sulphide Inclusions. Etched with nitric acid. $\times 1000$.



FIG. 17.—Similar to Fig. 16. Etched with nitric acid. $\times 1000$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.]

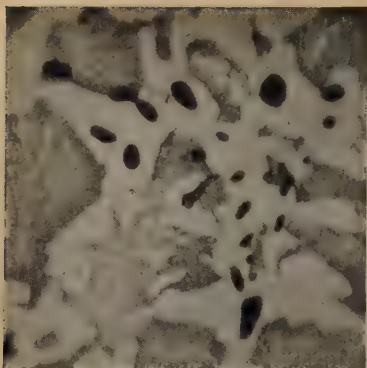


FIG. 18.—Similar Section to Fig. 16 after heating above A_{r3} and air-cooling; carbide migration into channels. Etched with nitric acid. $\times 1000$.

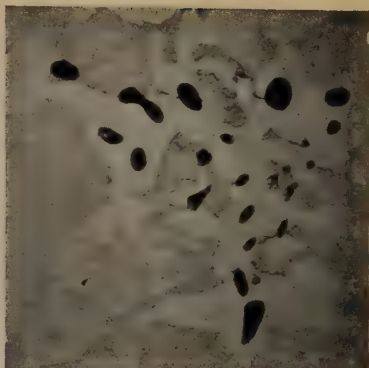


FIG. 19.—Same Field as Fig. 18. Etched with boiling alkaline sodium picrate. $\times 1000$.

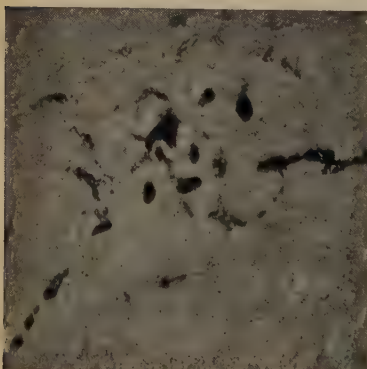


FIG. 20.—Similar Section to Fig. 16 heated above A_{r3} and water-quenched; martensitic structure in channel. Etched with nitric acid. $\times 1000$.

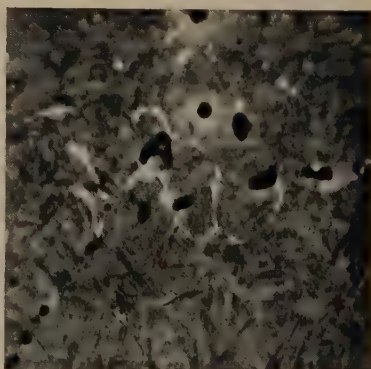


FIG. 21.—Same Field as Fig. 20; incomplete migration of carbide into channel. Etched with picrate. $\times 1000$.

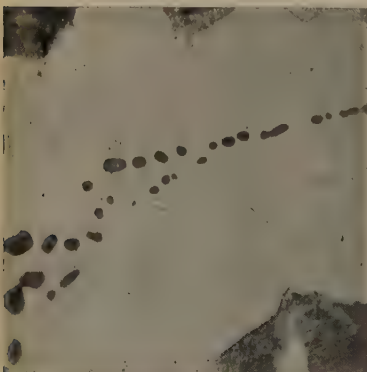


FIG. 22.—Similar Section to Fig. 20 reheated to same temperature and slowly cooled in furnace; expulsion of carbide from channels. Etched with nitric acid. $\times 1000$.

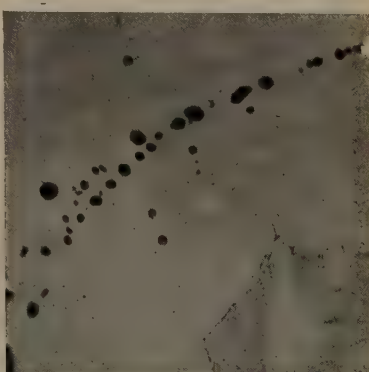


FIG. 23.—Same Field as Fig. 22. Etched with picrate. $\times 1000$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.]

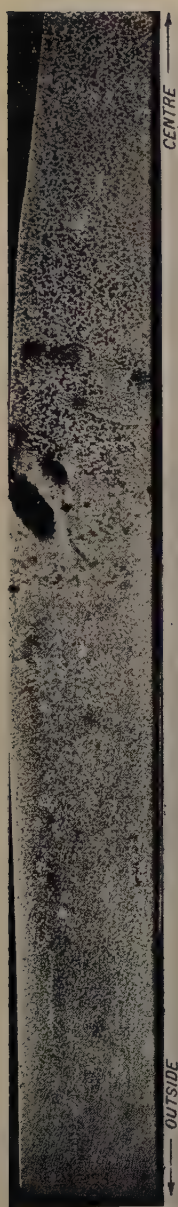


FIG. 24.—Macro-Etch of Slice of Ingot from outside to centre.



FIG. 25.—Sulphur Print of Slice of Ingot from outside to centre.



FIG. 26.—Typical Example of "Strings" and Envelopes round Pearlite Grains. Etched with nitric acid. $\times 1000$.



FIG. 27.—Another Example showing Envelopes round a Larger Pearlite Grain. Etched with nitric acid. $\times 1000$.

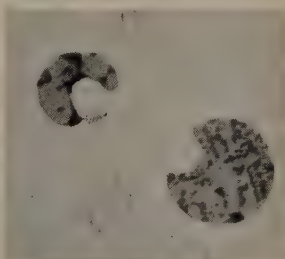


FIG. 28.—Typical Complex Sulphide Particles as found in rim and to some extent in core. Etched with nitric acid. $\times 1000$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.]

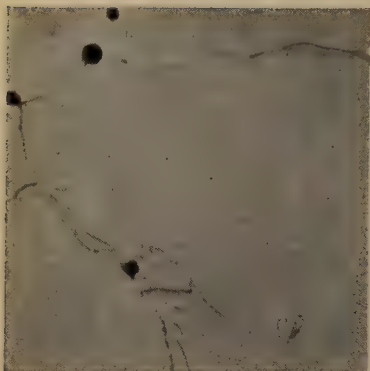


FIG. 29.—Readiness of String Material to Flow under Polishing. Etched with nitric acid. $\times 1000$.

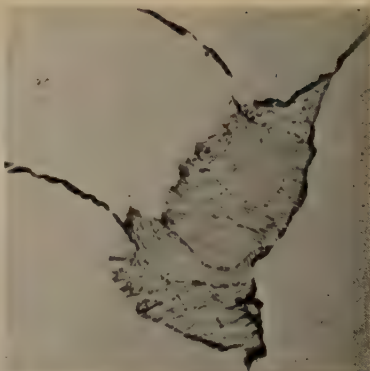


FIG. 30.—Typical Thick Envelope in Rim Portion of Ingot. Etched with alkaline sodium picrate. $\times 1000$.

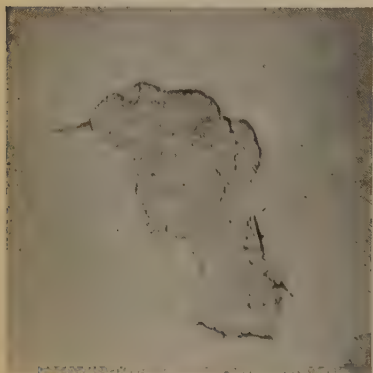


FIG. 31.—Slight Envelope Typical of Core. Etched with picrate. $\times 1000$.

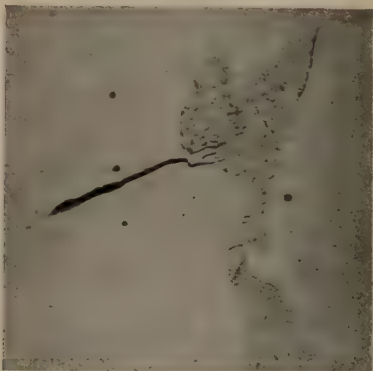


FIG. 32.—Typical of Ingot Centre; reappearance of "strings." Etched with picrate. $\times 1000$.

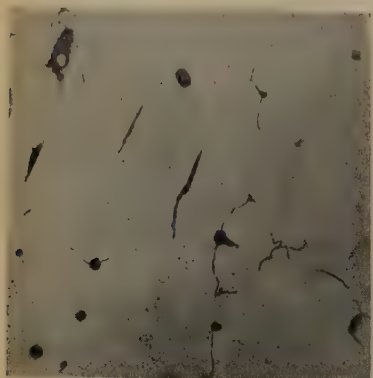


FIG. 33.—Typical General Structure in Centre of Rim. Etched with nitric acid. $\times 100$.



FIG. 34.—Similar Section to Fig. 33 heated to 1000°C ., water-quenched and annealed at 850°C .; reduction in thickness of strings. Etched with nitric acid. $\times 100$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.]

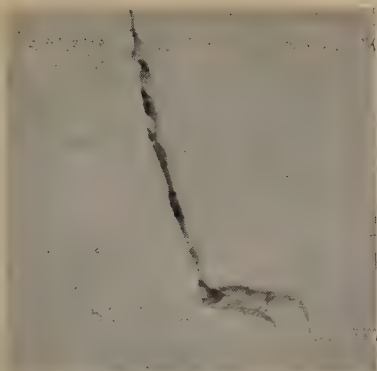


FIG. 35.—Portion of Same Field as Fig. 34. Etched with nitric acid. $\times 1000$.

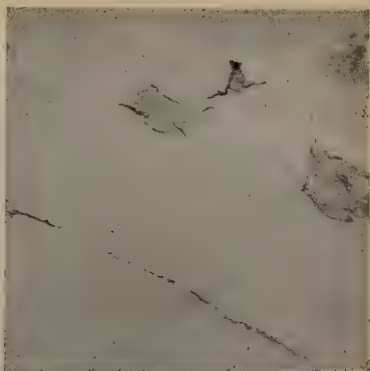


FIG. 36.—Similar Field to Fig. 34. Etched with alkaline sodium picrate. $\times 1000$.

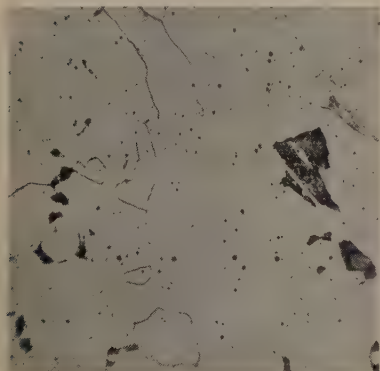


FIG. 37.—Typical Section in Rim; angular pearlite and scattered inclusions. Etched with nitric acid. $\times 100$.

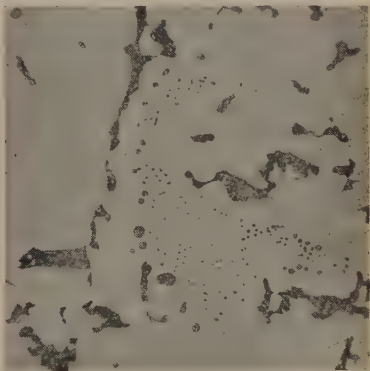


FIG. 38.—Typical Section in Centre of Core; more rounded pearlite and aggregation of inclusions. Etched with nitric acid. $\times 100$.

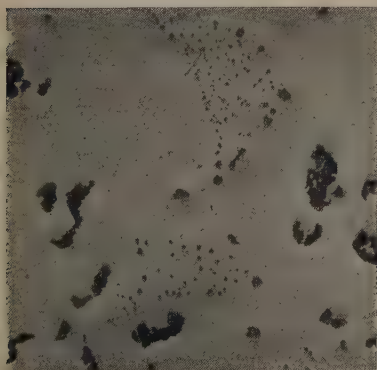


FIG. 39.—Typical Group of Inclusions in Centre of Core. Etched with nitric acid. $\times 100$.



FIG. 40.—Same Field as Fig. 39; phosphorus concentration. Etched by electrolytic soda attack. $\times 100$.

(Micrographs reduced to two-thirds linear in reproduction.)

[Law and Harbord.]

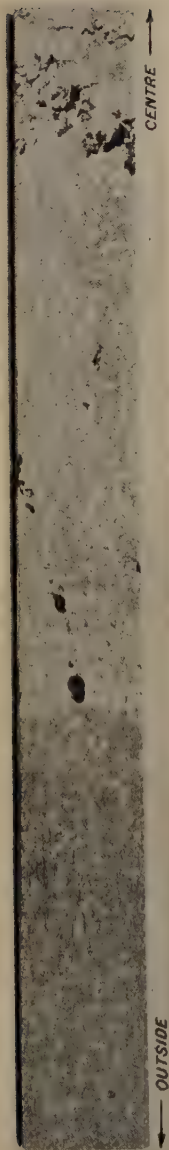


FIG. 41.—Macro-Etch of Slice of Ingot from outside to centre.



FIG. 42.—Sulphur Print of Slice of Ingot from outside to centre.



FIG. 43.—Typical Structure of Core. Etched with alkaline sodium picrate. $\times 100$.



FIG. 44.—Part of Same Field as Fig. 43. Etched with picrate. $\times 1000$.

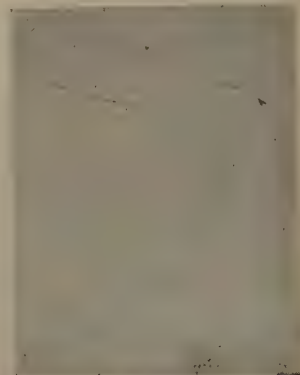


FIG. 45.—Typical Section after Annealing and Slow Cooling; reduction of string material without pearlite formation. Etched with picrate. $\times 1000$.



FIG. 46.—Typical String. Etched with sodium benzoate. $\times 1000$.

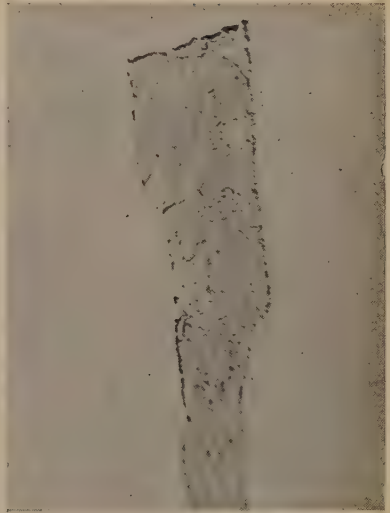


FIG. 47.—Typical Pearlite in Thin Envelope. Etched with benzoate. $\times 1000$.

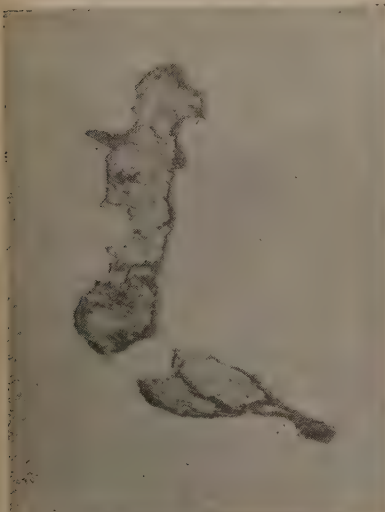


FIG. 48.—Typical Pearlite in Thick Envelope. Etched with benzoate. $\times 1000$.



FIG. 49.—Type of "Stepping" in Strings. Etched with benzoate. $\times 1000$.

(Micrographs reduced to two-thirds linear in reproduction.)

solution in channels containing sulphide particles, as was found in the killed ingot and as appears to some extent in the core of this ingot; the phosphorus appears in the rim with carbide in the form of strings and envelopes, as if it solidified as a definite constituent rather than as a solution with a gradually falling melting point.

INGOT-IRON INGOT No. 65.

In the hope that further light might be thrown upon this matter, work was started on the ingot-iron ingot No. 65, as it was thought that an examination of this with its low phosphorus content might help to elucidate the observations made on ingot No. 59.

The composition of ingot No. 65 was as follows :

Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0.050%	Trace	0.017%	0.005%	0.050%

The essential difference between this ingot and No. 59 from a chemical standpoint and from the point of view of the investigation is the very low phosphorus content, while other constituents, with the exception of manganese, are fairly similar. This ingot had a clearly defined rim as shown by macro-etching and sulphur-printing (Figs. 41 and 42). The section from outside to centre of the ingot was cut into 16 micro-sections, marked *A* to *P*, the end of the rim appearing to be about the mid-point of section *G*.

The outstanding feature of this ingot under micro-examination was that, although macro-etching showed the limits of the rim clearly, there was practically no structural change between the rim and the interior, with the exception that there was a marked and sudden increase of sulphide particles.

Other interesting features were :

(1) There was practically no pearlite in any part of the ingot, the carbide present being in the form of strings, as in the rim portion of No. 59; such occasional small pearlite areas as did exist were surrounded by envelopes.

(2) Although the carbon content was the same in both ingots, the amount of pearlitic carbon and strings of carbide material was far less in this ingot; this is considered to be a further confirmation that the strings and envelopes in ingot No. 59 were not composed of cementite alone, and, in view of the higher phosphorus content of that ingot, is suggestive that much of that material was phosphide in some form.

(3) Sulphide particles were not of complex character, but, as might be expected with a low manganese content, were MnS partially and in some cases completely surrounded by FeS.

(4) There was some slight sign of more "carbide" strings

in pieces between the rim and ingot centre. Figs. 43 and 44 show a typical structure taken in the core of this ingot at low and high magnification, respectively.

Specimens both from the rim and from the interior of the ingot were very slowly annealed. The "carbide" material had almost entirely disappeared without any sign of the production of pearlite in its place, thus throwing further doubt on the genuineness of this "carbide" (Fig. 45). Whereas samples from ingot No. 59 treated in a similar way showed a decrease of carbide with an increase of pearlite, this was not so with the ingot-iron ingot.

The possible explanation for this may be that the content of phosphorus is so low that even under slow cooling carbide is not driven away from the phosphide as in the killed ingot, but that the carbo-phosphide material remains undecomposed but dissolved in the surrounding ferrite.

At this stage in the investigation, work was stopped by the outbreak of war, and it has only quite recently been possible to give any further time to the research. On resumption, further efforts were made to find some means of establishing the nature of the strings and envelopes found in the rimmed and ingot-iron ingots. Eventually alkaline sodium benzoate, originally suggested by Thompson and Whitehead,¹ was found to be the most satisfactory reagent for this purpose.

According to Thompson and Whitehead, boiling alkaline sodium benzoate darkens carbide in a similar manner to alkaline sodium picrate, and for that reason its value as an etching reagent had not been seriously investigated earlier. As, however, its action was stated to be much slower, it seemed possible that it might be more capable than alkaline sodium picrate of differentiating between carbide and phosphide in steel. It was found that when using Thompson and Whitehead's standard benzoate solution the strings in sections cut from the rimmed ingot were completely blackened in 2 min., whereas, according to Thompson, even coarsely laminated pearlite is darkened only after $\frac{1}{2}$ – $\frac{3}{4}$ hr. Various modifications of the solution were made, greatly reducing the excess alkalinity, until results were obtained in which the strings were slightly coloured in 2–3 min. Figs. 46, 47 and 48 respectively show examples of strings, pearlite with a thin envelope, and pearlite surrounded by a thick envelope in sections of the rimmed ingot etched in this manner. Quite frequently the strings assume a curious "step" formation, which is worth recording and is shown in Fig. 49.

It was found that the carbide lamellæ in the rimmed and Armco ingots were slightly tinted by this solution; on the other hand, carbide lamellæ in sections of the killed ingot No. 36 were not coloured by prolonged etching, but were only slightly darkened by boiling in the original Thompson solution for 15–20 min.

¹ *Transactions of the Faraday Society*, 1923–24, vol. 19, p. 152.

This definitely seemed to show :

(1) That the string material in the rimmed and ingot-iron ingots was not normal cementite.

(2) That the cementite lamellæ in the pearlite of the rimmed and ingot-iron ingots was of a different composition from the carbide lamellæ of the killed ingot.

In these notes distinction has been made between ingots Nos. 36 and 59, as-killed and rimmed, respectively, as it was naturally thought that such differences as were found in their structure were due to the rimming action in the latter. This impression was strengthened when it was found that the differences were more marked in the rim than in the core; in parts of the latter some evidence of similarity to the killed ingot was found in the form of channelling and grouping of inclusions. When, however, the ingot-iron ingot was examined and found to have no structural difference between rim and core, although the ingot showed a well-defined rim and the carbide formation throughout was typical of the rim in ingot No. 59 and totally different from ingot No. 36, the question arose as to whether the unusual characteristics in carbide formation found in the rim of No. 59 and throughout the ingot-iron ingot did in fact result from the rimming action, or were due to some other cause. This question still remains to be settled.

SULPHUR.

The behaviour of sulphur during the solidification of ingots, which was the original object of this research, has been to a considerable extent side-tracked in the investigation of the other questions dealt with in these notes, but the following remarks may be of interest.

Killed-Steel Ingot No. 36.

In this ingot the sulphide occurs throughout as normal manganese sulphide. Complex sulphide particles were rare if not actually non-existent. As might be expected, the particles were smallest near the ingot wall, and increased in size in the more slowly cooled parts of the steel, where they were almost entirely situated in the channels, tending to collect together in the centre of the widest of these, or in the junction of two or more channels (Figs. 5 and 6, 9 and 16). It is only in the more rapidly cooled parts that sulphide particles were found embedded in pearlite grains, as shown in Figs. 9 and 12 near the outside of the ingot. It seems clear, therefore, that sulphide particles solidify in the molten metal and are carried as solids in the mother-liquor, and finally take up their position in the last of the liquor to freeze; this being so, those sulphide inclusions which are found finally in the pearlite grains have been unable to reach their proper place in the channels owing to the speed at

which freezing has occurred, in which case it is logical to expect that some mother-liquor which is carrying these particles would be entrapped round the sulphide. Any such films of mother-liquor would contain phosphorus in solution, so that when the migration of carbon occurs in the solid ingot from the channel solution, it would be prevented from approaching the sulphide particles by the phosphorus content of the envelope of mother-liquor. This would account for the occurrence of ferrite material found round sulphide particles in pearlite grains, as shown in Fig. 12. These envelopes are usually very small, but can be seen in most cases to a limited extent, but on account of their small size it was not possible to confirm by etching that they were phosphoric. Although, therefore, this point has not been proved, the suggested explanation affords a logical reason for the existence of ferrite rings round trapped sulphide inclusions.

As regards the old problem of why manganese does not segregate with the sulphur, no direct positive evidence has been obtained. There is, however, a very considerable amount of evidence to show that sulphur freezes out originally in the form of iron sulphide, and changes in the solid state to manganese sulphide (if sufficient manganese is present). If this view is accepted, the exchange of bases from iron sulphide to manganese sulphide, by the extraction of manganese from surrounding ferrite-manganese solution, would account for the lack of any corresponding increase of manganese in the segregated sulphide parts of the ingot, as shown by chemical analysis.

Rimmed-Steel Ingot No. 59.

There appeared to be little similarity between the behaviour of sulphide in this ingot and in ingot No. 36, and except for that portion of the core where segregation was highest, there was no evidence of the agglomeration of particles into groups such as was found in the channels in ingot No. 36. It is perhaps significant that it was only in this part of the ingot that any evidence was found of a phosphide solution of varying phosphorus content similar to the channels in No. 36—see Figs. 38, 39 and 40. The only other observation was that the sulphide in the rim was practically all of complex type, with an increasing amount of normal manganese sulphide in the core. There was no evidence as to whether this was connected with the rimming action or merely a coincidence, but the fact that little complex-type sulphide was found in the ingot-iron ingot, in either the rim or the core, suggests that the latter was more likely to be the case.

Ingot-Iron Ingot No. 65.

Practically all the sulphide in this ingot was a mixture of iron sulphide and manganese sulphide, as would be expected from the low manganese content, and there was little of the duplex type as

found in ingot No. 59. There was no difference (except in quantity) between the rim and core, and the only point worthy of note was that the two sulphides appeared together in the same particle often with the MnS surrounded by FeS, thus showing that the two sulphides are not mutually soluble in one another in all proportions.

OBSERVATIONS AND GENERAL CONCLUSIONS.

In the first place the authors wish to make it quite clear that this investigation is far from complete; in their opinion a detailed examination of an ingot of similar composition to the rimmed ingot No. 59, but made from killed steel, would probably throw considerable light on many of the questions which have arisen, and would serve to show whether certain unexpected features which have been observed are attributable to the action of rimming or to the relative proportions of the various elements present. As, however, under present conditions it is not possible to obtain such an ingot, and if it were it is unlikely that sufficient time would be available for its investigation, they are putting forward a record of their work up to date, in the hope that it may help to fit in with the work of other investigators, and thus assist in elucidating some of the problems surrounding the freezing and cooling of ingots.

In their opinion the examination of ingot No. 36 has shown clearly the manner of solidification and subsequent changes in this ingot, and they are satisfied that their hypothesis is substantially correct. The investigation of ingots Nos. 59 and 65 demonstrates beyond doubt that in these low-carbon ingots, either as a result of their rimming action or of their composition, or both, the freezing is far more complex and differs materially from that in ingot No. 36.

Many problems present themselves, the most important of which may be summarised as follows :

(1) The material referred to as "strings" and "envelopes" and which the authors believe to be some form of carbon-phosphorus-iron combination undoubtedly exists; it is not free cementite; it does not appear in ingot No. 36; it occurs more markedly in the rim than in the core of ingot No. 59, but occurs uniformly throughout ingot No. 65. What are the conditions governing its formation and existence? Does this complex occur in ingot No. 36 and break down entirely, whilst its decomposition is incomplete in ingots Nos. 59 and 65?

(2) It seems clear from this research that the carbide lamellæ in the pearlite in ingot No. 36 are different from those in ingots Nos. 59 and 65, the composition of the latter apparently being more similar to that of the strings and envelopes, *i.e.*, the iron-carbide-phosphorus constituent, whereas the former appear to be pure carbide; no doubt, the explanation to question No. 1 would also assist in explaining this.

(3) What are the controlling factors in the formation of the varying types of sulphide in ingot No. 59? Is the complex form brought about by the rimming action, and, if so, why does it not occur in the rimmed portion of ingot No. 65?

With the exception of ingot No. 36, in which their study of the structure suggested the probable course of events during freezing and cooling, the authors have not put forward any hypotheses to explain their observations. In the former case their suggested explanation fits in with theoretical considerations, is supported by all their observations and explains certain points which were formerly obscure. In the cases of ingots Nos. 59 and 65 the unusual features to which they have drawn attention, coupled with the incompleteness of the research and their inability to obtain a killed low-carbon ingot for comparison, have made impossible the drawing of any conclusions, and they have therefore confined themselves to a strict record of their detailed observations. The problem is of intense interest, and it is hoped that these notes will serve as a stepping-stone in the search towards the solution of this important and fascinating subject.

DISCUSSION.

Mr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett, Co. Durham) said: I have read the paper some three or four times for the reason that I find myself in almost entire disagreement with the authors' conclusions. They deal with the heterogeneity produced in three ingots by the segregating elements carbon, phosphorus and sulphur, and I will take phosphorus first. It is evident that the authors believe that when the critical range is entered the higher-phosphoric areas begin to drive the carbon in them as far away as possible, but I can see no reason for postulating any such pushing action; in eutectoid steels, for instance, the carbon is not ejected from areas rich in phosphorus. A much simpler explanation is that phosphorus raises the upper limit of the critical range, with the result that during cooling ferrite nuclei appear first in parts containing most phosphorus, and the ferrite then continues to be deposited there. Nor can I entertain the view that the primary crystals in ingot No. 36 were entirely free from phosphorus. The authors admit that phosphorus segregated in the "channels" and, as these would certainly contain more carbon than the primary crystals during solidification, it is not clear why they should consider that the process of differential freezing did not also operate on the phosphorus from the very start of solidification as one would expect. Apparently, it is the etching effects produced by cupric reagents and electrolytic soda attack which led the authors to that surprising

conclusion. Such effects, however, need cautious interpretation; account must be taken of marked differences which can be produced by relative concentrations. For instance, if two areas were in juxtaposition, one containing, say, 0.10% of phosphorus and the other 0.05%, the latter would be darkened by copper deposition, but that would not be the case if the other area contained 0.025%; the 0.05% area would then remain bright. The sharp line of division between the channel and the surrounding steel shown in Figs. 14 and 15 can be similarly explained as an etching effect, for, even if the primary crystals were phosphorus-free, the change should not be so abrupt, since phosphorus would undoubtedly diffuse slowly outwards as the ingot cooled down.

Turning now to the carbide, I would point out in the first place that, contrary to the authors' assertion, the carbon contents of ingots Nos. 59 and 65 were not the same, as can be seen from the analyses at the various positions in the ingots which have been recorded by the Ingot Committee. I myself witnessed the manufacture of ingot No. 65 and watched the bath being stewed for about 2 hr. after the carbon had dropped to 0.05%. Ingot No. 59 was a Bessemer steel, and as only a 2½-min. afterblow was given I feel reasonably certain that the carbon content of that ingot was at least 0.02% higher than that of No. 65, an amount which would account for the larger quantity of carbide observed in it. For some unstated reason the authors have seemingly abandoned the idea that the phosphorus drove the carbon away in these ingots, for they consider that a carbide-phosphide material is present in them. Now, as far as I am aware, carbide and phosphide of iron are not mutually soluble to any extent in the solid state, so that if free phosphide occurred along with the cementite in the envelopes and strings it should be readily detectable. In my opinion, however, the use of neither picrate nor benzoate of sodium as a staining reagent would enable that to be done with certainty. I have often observed that massive cementite in hypereutectoid steels exhibits colours merging from black to red and red to purple when treated for 5–15 min. in boiling sodium picrate. One informative test would be to determine the temperatures of the Ac_1 and Ar_1 points either pyrometrically or by quenching, since the presence of phosphide in any appreciable amount should affect them. I venture to assert that they would be found to be in their normal positions. In support of their contention that the envelopes and strings were composite in character the authors state that the carbide in ingot No. 59 was diminished in quantity after a specimen had been heated to 850° C. There, again, I am unconvinced, for that treatment refines the grains, with the result that the carbide occurs at many more grain boundaries and therefore in a much thinner condition. The fine films thus formed can sometimes be easily overlooked when ordinary etching reagents are used, as I have often found, but a cupric reagent, such as Le Chatelier's, makes them readily visible.

Finally, I have two remarks to make on the authors' observations on the sulphides. In the first place they state that the inclusion shown in Fig. 7 and also in Fig. 8 is MnS, but it looks remarkably like chromite. I would point out that the steel represented by ingot No. 36 was purposely made with a very oxidising slag, and under that condition some chromium, which is invariably present in iron, can be oxidised, as I have observed more than once. Idiomorphic crystals of MnS are usually in the dendritic form, and I consider that the authors should have made reasonably certain that these rhomboidal inclusions were actually MnS by examining their solubility in weak sulphuric acid. The other thing on which I wish to comment is the statement that practically all the sulphide in ingot No. 65 occurred as FeS and MnS. Some years ago a sample of the plates rolled from that particular cast was sent to me and I found very little MnS in it. There was, however, a considerable amount of FeO in association with the FeS. Unless some distinguishing test is applied FeO can easily be mistaken for MnO. One method is to cool a specimen fairly rapidly from about 1000° C., so as to form the characteristic FeO-FeS eutectic.

Dr. D. BINNIE (Lancashire Steel Corporation, Ltd., Irlam, near Manchester) said : The authors maintain that they have some form of a carbon-phosphorus-iron complex which occurs more markedly in the rim than in the core of ingot 59 but occurs uniformly throughout ingot 65.

The analyses of ingots 59 and 65 should be compared in more detail than by merely recording the pit analyses. Also, ingot 59 was a basic Bessemer rimming ingot of much higher nitrogen content than ingot 65, which was a basic open-hearth rimming ingot. I am not very sure that the difference in the nitrogen content can be ignored when comparing fine points in the two ingots.

However, if we examine the analysis at the rim (position *A*¹), just inside the core (position *F*) and at the centre of the ingot (position *C*), we find for the two ingots :

		Carbon. %.	Sulphur. %.	Phosphorus. %.	Manganese. %.	Nitrogen. %.
<i>Ingot 59.</i>						
Position	<i>A</i>	0.05	0.023	0.060	0.46	0.011
	<i>F</i>	0.07	0.083	0.181	0.53	...
	<i>C</i>	0.07	0.074	0.180	0.52	0.017
<i>Ingot 65.</i>						
Position	<i>A</i>	0.04	0.011	0.004	0.05	...
	<i>F</i>	0.04	0.025	0.007	0.06	...
	<i>C</i>	0.05	0.023	0.005	0.06	...

The authors' carbon-phosphorus-iron complex is, from their

¹ Positions *A*, *F* and *C* are three of the standard positions adopted by the Ingot Committee for taking samples from longitudinal medial sections of ingots (see Fourth Report on the Heterogeneity of Steel Ingots, Fig. 2, p. 8, *The Iron and Steel Institute*, 1932, *Special Report No. 2*).

evidence, only well-defined in the regions where the carbon is 0.05% or less, *i.e.*, throughout the locations where the carbon is too low for all of it to form well-defined pearlite.

Would the authors not think from the above analytical detail that the evidence for the existence of a carbon-phosphorus-iron complex should have been more apparent in the core of ingot 59, where the phosphorus has jumped up to 0.18%, rather than in the core of ingot 65, where the phosphorus percentage is low throughout—the reverse of what the authors observed?

Again, to establish the nature of the complex the authors heated a specimen from the rim of ingot 59 to 1000° C., but they do not say for how long the specimen was heated. In order to break up any phosphorus-rich zone in a steel I would have thought that 1000° C. would have been too low a temperature to give positive results. I suggest that the authors should have soaked the steel if possible within the δ -range, say, 1450° C. and above, in which any complex formed as a result of an insufficient sojourn in that range would most likely be removed.

In the literature on the distribution of substances between δ -iron and liquid iron, carbon and phosphorus alone of all the ordinary elements found in steel have the same ratio of the concentration in the solid phase to that in the equilibrium liquid phase. The initial degrees of separation of carbon and phosphorus from the melt might follow one another closely. Would this explanation, which results from the ordinary laws of differential freezing, not explain the apparent phenomenon of a carbon-phosphorus-iron complex?

Dr. L. NORTHCOTT (Teddington): I should like to refer to the question of phosphorus solubility. On p. 493 P the authors say "Primary crystals of ferrite (containing some of the manganese and silicon, and possibly some carbon in solution but not the greater portion) entirely free from phosphorus are the first to crystallise as a homogeneous solid solution." The phosphorus content of this steel is of the order of 0.02% or less, and according to the equilibrium diagram in the pure binary series about 1% of phosphorus is soluble in iron at a temperature of about 1000° C. If the authors have any justification for saying that they can obtain steel free from phosphorus they are on the verge of an epoch-making discovery, namely, how to get rid of phosphorus from high-phosphorus steels. Quite frankly, I see no justification whatever in the paper for the claim that the crystals that solidify are entirely free from phosphorus.

On the following page the authors say: ". . . the freezing of a killed ingot proceeds in accordance with theoretical considerations and the views held by the late Dr. J. E. Stead. Moreover, it confirms the existence of the 'iron-carbon-phosphorus complex' observed by Professor Andrew." I thought that the idea of the iron-carbon-phosphorus complex proposed by Professor Andrew

had been killed years ago. This complex was considered to be a solution high in carbon, phosphorus and sulphur, insoluble in liquid steel or liquid iron. In other words, it was a state of liquid immiscibility which I should think could be fairly readily shown by experiment. On the outbreak of war an investigation was being carried out to determine just what the limits of immiscibility were. Evidence was obtained of liquid immiscibility when sulphur and phosphorus were each present in quantities of the order of 2% or 3%, whereas in these killed ingots with which the authors are dealing something like 0.05% of sulphur and 0.016% of phosphorus were present. From the authors' results I see no justification for the statement that there is liquid insolubility owing to the presence of this complex.

On p. 497 P the authors say ". . . the phosphorus appears in the rim with carbide in the form of strings and envelopes, as if it solidified as a definite constituent rather than as a solution with a gradually falling melting point." I should like to draw their attention to the paper presented this morning by Mr. McLean and myself,¹ in which an attempt is made to show the primary structure of a rimmed-steel ingot by means of a copper reagent.

Dr. ING. W. WRAZEJ (London) : This paper contains the results of a great deal of work, but, in my opinion, it will be of little value if the microscopic constituents cannot be identified. Dr. Bradley, with whom I was working for some time, found difficulty in explaining the presence in an iron-nickel-aluminium alloy of two phases with slightly different α -iron lattice parameters. X-ray spectrograms showed no difference in the low-angle reflections for either phase. At high angles the reflections from 220 differed very slightly, but 331 showed distinct $K\alpha_1$ and $K\alpha_2$ doublets for both phases. Beside them the superlattice appeared for one of the phases. Micro-examination at a magnification of 4000 diameters distinguished very clearly between the structural components. If a component is revealed by X-ray examination that should be accepted as really good evidence, and I think that the structure with which this paper deals could be found by X-rays. X-ray investigation will differentiate distinctly between pure cementite and a carbon-phosphorus-iron complex. Even very minute quantities of cementite in an iron sample produce pronounced individual lines in the X-ray spectrogram, which can easily be distinguished from the lines of other iron-carbon components. Such components can, if necessary, be examined by spectrographic analysis by Dr. Convey's excellent method.

In my opinion the older metallographic methods, using different etching reagents to distinguish the micro-features, though useful in many ways, are not accurate enough nowadays for such purposes.

¹ "The Structure and Segregation of Two Ingots of Ingot Iron, One Containing Lead," this volume, p. 429 P.

Picrate etching is very sure in revealing cementite, but it is not suitable for determining differences between the iron-carbon and other alloy components.

Dr. C. H. DESCH, F.R.S. (Vice-President; London): The criticisms put forward by Mr. Whiteley will be considered by the authors. I must say that I found this paper very interesting. I saw this work when it was being done some years ago, and the plan of making a detailed microscopic study of a section right across the ingot was good. It will have to be developed and applied more frequently. There are certain changes in the microstructure, not merely in the macrostructure, which will have to be accounted for. Since this paper was prepared, the Ingot Committee have had other examples of similar changes in structure not accounted for by the change from columnar to equi-axed crystals.

Having examined the original photographs which the authors prepared—which showed more than these reproductions do—I thought they had good evidence for assuming a difference between these stringers and the ordinary films of cementite. It is not only a question of etching. One can get more definite results, I think, by dealing with alkaline etching reagents than Mr. Whiteley admits. There were also distinct differences in hardness, as mentioned in the paper. It is true that according to the equilibrium diagram these small quantities of phosphorus in the δ state should be in solid solution and should have no tendency to separate. But we know that even at those high temperatures, although the equilibrium between the iron and carbon is reached rapidly, that between the iron and phosphorus is not reached so rapidly. There is a fundamental difference between the two. Whilst phosphorus atoms take up a place on the iron lattice, the carbon is interstitial, and with ordinary rates of cooling the departure from the equilibrium in an iron-phosphorus solution, even with high temperatures, may be comparatively large. I remember that amongst the early ingots examined by the Ingot Committee was a large one which had been cast in sand, and in that the segregation of phosphorus was remarkably high. I do not think that the ingot was kept, so it is not possible to make an examination of this kind on critical portions, but, to judge by photographs, the apparently low phosphorus segregated to quite a big extent. I think that there is more to be said for the authors' conclusions than some of the critics would perhaps allow.

As regards the supposed manganese sulphide inclusions, I seem to recollect that years ago Baykoff published many photographs of manganese sulphide crystals, some of which had this angular form. In those days, contamination by chromium was much less likely. Mr. Whiteley has suggested a simple test, and I hope that the authors will apply it.

I suggest that a detailed study of sections right across an ingot

of this kind will bring to light many unsuspected differences between different parts of the ingot. I know that the authors have not had an opportunity of following up the work as they would like to do, and they are not dogmatic about their conclusions. They have put forward something which can be discussed, and I hope that other ingots will be examined in similar detail.

Dr. T. SWINDEN (Member of Council; The United Steel Companies, Ltd., Stocksbridge, near Sheffield): May I ask a question concerning the suggestion that it would be desirable to examine an ingot of a similar composition to No. 59 but made from killed steel? How do the authors suggest that that should be done? It seems to me that the very fact of killing the steel would fundamentally affect all the other characteristics. From the point of view of the paper, it would be desirable if one could visualise such a material, but the point of my comment is that it is a physical impossibility.

AUTHORS' REPLY.

The AUTHORS wrote in reply: When we decided, with considerable reluctance, to publish our observations on the structure of these three ingots we did so, not because those observations provided any scope for discussion, but because we had reached an impasse with the means at our disposal and we hoped that someone with greater facilities for carrying out research might continue the work or, at least, that some suggestions might be made for carrying it a stage further.

Dr. Wrazej has made the most profitable contribution when he suggests that X-ray examination should be capable of distinguishing between constituents which occur in very small quantities. We are in complete agreement with him when he says that the older metallographic methods are not accurate enough nowadays. When magnifications exceed 1000 diameters that is certainly true.

Unfortunately, we have no X-ray apparatus at our disposal and—what is even more unfortunate—we have not the skill or experience to use it, so that this work must be left to others. We sincerely hope, however, that the work will be undertaken, and if we can render any assistance we will gladly do so.

Dr. Binnie, while not making any suggestions for the solution of the problem, calls attention to one or two points which will have to be considered in future work. First, the question of nitrogen. Apart from the well-known "nitride needles," far too little is known of the effect of nitrogen in steel. Similarly, arsenic does not appear to have been even determined in these ingots, and one (No. 65)

contains no less than 0.16% of copper. We are inclined to think that these constituents do not materially affect the structure, but that is only a belief which will have to be proved or disproved. The second point raised by Dr. Binnie is the suggestion that there is a lower limit of carbon beyond which "the carbon is too low for all of it to form well-defined pearlite." In the course of our experience we must have examined a large number of low-carbon steels or irons, but we cannot recall having come across a case where this was apparent. It is an interesting point, however, and another of those problems which remain to be solved. In any case, it does not seem to explain the presence of the envelopes surrounding well-defined pearlite, and the carbon limit would have to be raised to at least 0.07% and not 0.05%.

Dr. Binnie says that "the authors maintain that they have some form of a carbon-phosphorus-iron complex," but that is surely a decided over-statement of the case. What we do maintain is that there is a constituent in these two ingots which bears no resemblance to iron carbide except a very superficial appearance, and we want somebody to tell us what it is, as we have failed to find the necessary proof for ourselves. We have suggested that it *may* contain phosphorus, but we want it proved—not in theory, but in fact.

We are sorry to note the evident tone of satisfaction in which Dr. Northcott declares that he thought Professor Andrew's "iron-carbon-phosphorus complex" had been killed years ago, and we can imagine his dismay when he

". . . saw the Dead on the river bed,
For the faithless stream was dry."

But we can bid him be of good cheer, for in this case the murder was really only a dream, and, even if Dr. Northcott shared in that dream, it will never be recorded that

"Dr. Northcott walked between
With gyves upon his wrists."

Rather do we look forward to happier times, not too far distant, when we can meet Dr. Northcott in friendly discussion and

"see truth dawn together—truth that peeps
Over the glass's edge when dinner's done."

But, in the meantime, why so much difficulty in imagining that steel freezes as other metals do? There appears to be some doubt as to the views held by Dr. Stead, with which we profess agreement, and it may, therefore, be well to quote his exact words. Referring to a cooling mass of molten steel he spoke of "a time when it consisted of crystallites of solid and nearly pure iron mixed with a liquid of lower melting point containing the bulk of the metalloids—a transitory condition all steels passed through when at a tempera-

ture below the first solidification point or liquidus and near the solidus point shown on the equilibrium diagram of the alloy of iron and carbon.”¹ That he included carbon in the metalloids is made quite clear when he refers later to the “liquid rich in carbon, sulphur and phosphorus.” Surely that is a perfectly logical conception.

If it were possible to carry out the Pattinson process on a mass of molten steel it is only reasonable to suppose that relatively pure iron could be ladled out and a mother-liquor rich in carbon and phosphorus left behind. In fact it has been repeatedly demonstrated that if an ingot is clogged before the centre is solid, the purer metal first freezing is consolidated, while the metal rich in carbon and phosphorus is squeezed towards the centre and up the pipe, thereby leaving an ingot with a centre lower in impurities than the outside—the converse of a rimmed ingot. In Professor Andrews’ diminutive ingot, natural contraction would appear to have performed the same function as clogging in a larger ingot, and the impure lower-melting-point material had been extruded from the top of the ingot. From this it requires no stretch of the imagination to picture the same action taking place in a rimming ingot. The escaping gas cannot travel outwards but must perforce travel inwards, and in doing so drives before it the still molten mother-liquor as the purer iron solidifies.

Mr. Mitchell has evidently had the same mental picture of the solidification of a rimming ingot, for in his paper on rimming steel,² he says “the author suggests that the solid rim is the result of two distinct processes: (a) Solidification of some liquor of average composition *in situ* due to local temperature, *i.e.*, normal crystallisation of material from the mother-liquor, and (b) the deposition of iron particles of high relative purity which are the product of the iron-oxide/carbon reaction.” The only qualification which we would make is that in our opinion the second factor is of minor importance and that if it were possible to have the gas evolution without any chemical reaction, the result would be the same. In other words, whether segregation is modified by the evolution of gas or not, it is a mechanical process. The fact that an inert added material such as lead segregates in the same way as other impurities is additional evidence in support of this view.

The theoretical solubility of phosphorus in iron and its practical insolubility seem to be a stumbling block to Dr. Northcott, but it is not a unique example. Tin is soluble in copper to an extent of no less than 8%, but it is the copper that separates first on freezing. And if phosphorus is so soluble in iron, how can the high-phosphorus segregations or “ghosts” occurring in low-phosphorus ingots and forgings be explained? Perhaps the iron-carbon-phosphorus complex is not so soluble after all!

We greatly appreciate the remarks of Dr. Desch, and are gratified

¹ *Journal of the Iron and Steel Institute*, 1912, No. II., p. 49.

² *Journal of the Iron and Steel Institute*, 1942, II., p. 340 p.

to learn that he is in agreement with us as to the desirability of studying the structure of ingots in more detail than has hitherto been done.

Dr. Swinden draws attention to a mistake in the paper which we had overlooked. We refer to an ingot of similar composition to No. 59, but made from killed steel; we should have said of similar composition but non-rimming.

Mr. Whiteley's contribution is entirely unhelpful and it is not easy to understand its purpose. He says he has read the paper three or four times and does not agree with our conclusions. Had he persisted in any one of the three or four attempts until he reached the last page he would have discovered that, with one very minor exception, we have found it impossible to draw conclusions "and we therefore confined ourselves to a strict record of our detailed observations." There is very little therefore with which Mr. Whiteley is in a position to agree or disagree.

Mr. Whiteley's digression into the subject of elementary metallography is interesting and some of his revelations are illuminating. First, he states that "idiomorphic crystals of MnS are usually in the dendritic form" and can be identified by their solubility in weak sulphuric acid. Mr. Whiteley might be reminded that the decomposition of manganese sulphide by weak sulphuric acid was known to at least one of us (E. F. L.) forty years ago, and he described the method of identification in a paper before the Institute thirty-six years ago.¹ Secondly, the statement that FeO can easily be mistaken for MnS —that is a mistake which the authors would not expect the most elementary student of metallography to make. Thirdly, Mr. Whiteley confesses that he has not been successful with the alkaline reagents. We can assure him that if he will persevere until he has mastered the technique of their use, he will find them extremely useful, consistent and reliable as Dr. Desch has pointed out. Finally, Mr. Whiteley attempts to interpret reproductions of the authors' photographs for them; after the classical case of the ginger-nut biscuit, this is a mistake which it was thought would never be made again.

In conclusion, when Mr. Whiteley has repeated our work and found it incorrect, we shall be very happy to discuss the matter with him.

¹ E. F. Law, *Journal of The Iron and Steel Institute*, 1907, No. II., p. 94.

A STUDY OF AUSTENITIC GRAIN GROWTH IN MEDIUM-CARBON STEELS.*

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(Figs. 14 to 83 = Plates XXXIX. to XLVIII.)

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SUMMARY.

A detailed investigation has been made of austenitic grain growth in unstrained medium-carbon steels throughout the whole of the temperature range between the Ac_1 and the solidus point. To ascertain the positions of the austenite grain boundaries at the temperature of heating the ferrite precipitation method was used, since it was found to be reliable and without any restriction in application. To record the grain sizes thus disclosed the counting method was largely employed, in which the average number of grains present in 10 sq. in. at a magnification of 100 is taken as the standard of comparison. The steels examined fall for the most part into two categories, *viz.*, coarse-grained and fine-grained, the latter type being produced by the addition of 1 lb. per ton of aluminium to the metal when in the ladle. Intermediate types could not be obtained simply by adding lesser amounts of aluminium. Eight interdependent factors were found to influence growth, *viz.*: Temperature, length and rate of heating; initial grain size, hot-work and the aluminium content of the steel; the rate of cooling from the solidus to 1200°C . and the state of the carbide. The manganese content of the steel may be yet another factor. With so many possible combinations an exhaustive examination of the subject was impracticable, but from the work done the conclusion may be drawn that any particular grain size formed by heat treatment in a given medium-carbon steel is the result of the concerted action of these various factors. It is shown that grain refinement takes place almost entirely at the Ac_1 transformation and is completed during the passage through the critical range. In the coarse-grained steels the rate of growth then steadily increased with the temperature of heating, and below about 1100°C . a state of virtual stability was eventually reached. In the fine-grained steels a remarkable halt in grain development occurred almost immediately after the refinement. Below 900°C . this period of inactivity was indefinitely long, and, as a consequence, the steel was fine-grained in character. Above 900°C . the halt became progressively shorter, but at any one temperature its actual duration could be varied widely by changing the rate of heating, the initial grain size and other factors. When once the halt was passed mixed grain sizes began to appear, consisting of large dominant grains embedded in small ones. Dominant growth of a relatively few grains was an effect also observed in coarse-grained steels, but the small grains did not remain so inactive. As the tem-

* Received June 30, 1943. This paper is published by authority of the Alloy Steels Research Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

perature was raised the mixed grain sizes gradually disappeared. After refinement by forging, a smaller grain size grew in coarse-grained steels at temperatures up to at least 1000°C . than after an equal refinement by heat treatment, and it is shown that the disparity was not due to differences between the banded heterogeneity or to the distribution of the inclusions. Hot-work seemed to be the cause. In fine-grained steels this factor was not so much in evidence, owing to the mixed grain sizes which were formed in the temperature range where it operated. The production of a coarse-grained steel was found to depend on the rate of cooling from either the liquid or solid condition to 1200°C . Unless the rate was fairly slow the steel was fine-grained in character. In the absence of manganese the change to the coarse-grained type could not be induced even by a very slow cooling. The state of the carbide had an important influence both on the extent of growth and on the length of the halt. Complete spheroidisation of the pearlite greatly minimised growth, especially in fine-grained steels. The effects of quenching and of quenching and tempering on growth were not the same as those of spheroidisation. Shortly after the first halt in well-tempered pieces with a large initial grain size a second halt occurred which persisted for a long while to above 1050°C . Attempts were made to convert solid coarse-grained steels into fine-grained by diffusing aluminium into them, but the results were inconclusive.

DURING the last decade or two grain growth within the completely austenitic range has been a prominent subject of investigation. In America, especially, both the control of grain size and its influence on various physical properties have been intensively studied by metallurgists, and to them much credit is due for the considerable advance which has accrued. The fact that a stipulated grain size is now not uncommonly included in specifications is an indication of the progress achieved. Yet, notwithstanding the large amount of work which had been done much remained obscure when the present enquiry began about seven years ago. Little was known with any degree of certainty as to the factors governing grain development in unstrained steels except that the addition of small amounts of alloys such as aluminium or vanadium retarded growth, and, even yet, no complete agreement has been reached on their mode of operation. The explanation most in vogue is that oxygen is the primary cause. It is asserted that when the steel at tapping contains an appreciable quantity of that impurity, extremely fine oxide particles of the added elements are formed and dispersed throughout the metal. These then serve both as nucleation centres and as inhibitors of grain growth. The evidence in support of this theory was well summarised some years ago by Bain.⁽¹⁾ Although the arguments that he advanced are impressive it is nevertheless difficult to see how fine inclusions can bring about many of the growth effects described in the following Sections. Taken as a whole, the results suggest rather that the state and character of the carbide as the critical range is entered are among the main determining factors.

SECTION 1, *containing Various Introductory Remarks.*

In the study of austenitic grain growth a trustworthy means of revealing the grain size existing at the temperature of heating is, of course, an essential requirement. Fortunately, several methods are now available details of which have been published at various times. An excellent summary by Ward and Dorn⁽²⁾ may be mentioned. One of the latest procedures to be devised is that of heat-etching in an inert atmosphere.⁽³⁾ While each of the methods has some specific advantage, none is without a drawback of one kind or another. Even the well-known carburising test has limitations. It is of little use at temperatures below 900° C., because a cementite network cannot there be readily produced, owing to the slow rate of carbon absorption. For the same reason the method is not suitable for the study of initial grain growth at any temperature. Moreover, the assumption is made, no doubt correctly in most cases, that the introduction of carbon causes no alteration in grain development. The alternative method of ferrite precipitation happens to be free from these particular disabilities. As in the carburising test, reliance is there placed on the deposition at the grain boundaries of the phase which separates as the steel approaches the Ar_1 point, and, since in medium-carbon steels that phase is ferrite, the method is applicable to them at all temperatures within the austenitic range, whether the heating periods be long or short. It thus appeared to meet the needs of the present investigation and was accordingly adopted. In using the method one precaution has to be taken which is of less importance in the carburising test. To obtain satisfactory results it is necessary to regulate the rate of cooling so that only a fairly thin network is formed, for if too much ferrite is precipitated the delineation of the smaller grains may be marred.

The subject of grain growth can seldom be adequately treated without the aid of photographic illustrations, but, while these are unquestionably desirable, their number may rapidly become excessive, especially when the work is extensive. This difficulty is not insuperable, however, for many grain sizes can be recorded numerically, and in preparing this paper there was no option but to employ that method as much as possible. Each figure given in the Tables denotes the average number of grains in a standard area of 10 sq. in. at a magnification of 100 diameters, so that by reference to the A.S.T.M. chart the size can readily be visualised. It should be observed that differences considerably less than those indicated by consecutive numbers on the above-mentioned chart can easily be detected, particularly when the comparison is made between specimens mounted side by side. In cases where two grain sizes were very similar, counting was often of value in enabling a decision to be reached. The procedure in applying the method was as follows : The field was projected on to the ground-glass screen of the camera

attached to the microscope, and as each grain was there counted it was spotted with ink to ensure that none was included twice; the number of the marginal grains not entirely in view was, of course, halved. At least ten fields taken at random were thus dealt with, and the average for the standard area was then calculated. Unless otherwise stated the grain sizes recorded in this paper were approximately uniform. With mixed sizes the method is not generally suitable, although it was occasionally serviceable.

Particulars of the steels on which much of the work was done are given in Table I. In every instance the sample was taken from a bloom or billet rolled from the lower half of the ingot. The majority of the steels were made in the acid open-hearth furnace under a fairly standard practice in which the FeO content of the slag was reduced to 19% or less at tapping by limestone additions during the boiling period. Several basic-steel samples other than those included in Table I. were also employed, but chiefly for checking the results obtained on the acid steels, and since the agreement was good there will be no need to mention them again. For the most part the steels enumerated in Table I. can be divided into two very distinct classes according to their behaviour in the McQuaid-Ehn carburising test. Samples 1, 2, 3, 3A, 4, 9 and 10 contained little or no aluminium and showed a grain size in the vicinity of No. 3, whereas a No. 7 size appeared in Nos. 3D, 3E, 5, 6, 7 and 8. It should here be emphasised that throughout the paper the terms coarse-grained and fine-grained are exclusively used to denote respectively these two classes.

When examining grain growth at temperatures up to 1150° C., the specimens were heated in a horizontal electric furnace wound with Kanthal wire so spaced that along one half a uniform temperature could be maintained while along the other half it steadily diminished to below 600° C. The gradient end was of advantage in several ways, as, for instance, in cases where the specimen was to be subjected to a rapid temperature change. Tests above 1150° C. were usually carried out in a Silit-rod furnace. Except when the heating period to be given was very short, the specimens were placed in silica tubes 11 in. long, fused at one end, the other end being closed with clipped rubber tubing. Decarburisation to any appreciable extent was avoided either by putting in extra pieces or else by the addition of a small quantity of high-carbon steel drillings.

In dealing with the influence of the speed of heating on grain growth three widely separated rates were generally employed, and throughout the paper they are designated as slow, rapid and very rapid. Since these terms frequently occur it will be as well to state their precise meaning at the outset :

“Slow heating” signifies that the temperature was raised through the critical range at from 6° to 8° C. per min., and when a rate is not mentioned this one is always implied.

TABLE I.—Description of Samples.

No.	Type of Steel.	Alu- minum added per Ton. Oz.	Class.	Condition.	Analysis. %.					Slag Iron. %.
					Carbon.	Silicon.	Phos- phorus.	Sulphur.	Man- ganese.	
1	Acid open-hearth	Nil	Coarse-grained	Billet	0.45	0.12	0.044	0.033	0.71	14.4
2	"	Nil	"	"	0.45	0.14	0.033	0.045	0.72	14.8
3	"	Nil	"	"	0.44	0.10	0.042	0.034	0.63	12.6
3A	"	1	"	"
3B	"	3	Mixed-grained	"
3C	"	9	"	"
3D	"	16	"	"
3E	"	32	Fine-grained	"
4	Basic open-hearth	3	"	"	0.44	0.11	0.012	0.043	0.63	9.6
5	Acid open-hearth	16	Coarse-grained	"	0.475	0.23	0.033	0.038	0.71	13.0
6	"	16	Fine-grained	"	0.42	0.21	0.027	0.037	0.63	12.7
7	"	16	"	{ Bloom Billet }	0.465	0.18	0.040	0.055	0.75	14.7
8	"	16	"	Billet	0.44	0.20	0.037	0.038	0.65	14.1
9	"	Nil	"	{ Pit sample Billet }	0.48	0.11	0.035	0.048	0.80	13.1
10	Basic open-hearth	Nil	Coarse-grained	{ Pit sample Billet }	0.45	0.24	0.036	0.031	0.88	8.3

"Rapid heating" denotes an average temperature rise of between 300° and 500° C. per min., to obtain which the tube containing the specimen was inserted in the furnace at or near the temperature of the test; in such tests specimens weighing less than 2 g. were taken.

"Very rapid heating" indicates an average temperature rise of about 800° C. per min. The specimen weighed approximately 0.2 g. and was roughly in the form of a cube. It was placed at the clipped end of the tube and afterwards dropped quickly on to one or more slowly heated specimens as soon as the required temperature was reached.

Since rapid and very rapid heatings necessitated the use of small specimens, it was clearly of importance to ascertain at the outset that grain growth was not affected by mass. Several tests were therefore carried out, on both coarse- and fine-grained steels, in each of which a hermetically sealed 3-lb. block containing two specimens of the same steel, weighing 0.2 and 0.8 g., was heated at temperatures between 950° and 1100° C. In no instance was there any observable difference between the grain sizes which developed in the specimens and in the block. As an example, Table II. shows the grain sizes

TABLE II.—*Experiment on the Effect of Mass on Grain Growth.*

	Average Number of Grains in 10 sq. in. at 100 Magnification.
Sample No. 4 :	
0.2-g. specimen	39
0.8-g. specimen	40
Block adjacent to base of drilled hole . . .	40

produced in sample No. 4 when treated in this way, the structures in all three pieces being similar to that illustrated in Fig. 36. Thus the experimental evidence demonstrated that mass of itself was not a factor concerned in growth, and consequently it received no further attention.

Although ferrite precipitation is frequently employed for the delineation of austenitic grains, the validity of the method seems to have been taken for granted. Certainly with medium-carbon steels it reveals grain sizes corresponding closely with those brought out by the carburising test, as the illustrations on the A.S.T.M. standard chart indicate. During the present investigation the two methods were compared a number of times both at 930° and at 1000° C. Typical examples of the results obtained at the latter temperature are given in Table III. In each instance the two specimens were heated together for 4 hr., the carburised one being then furnace-cooled and the other air-cooled. Although the agreement was always satisfactory, it nevertheless seemed desirable

to establish the reliability of the ferrite-precipitation method in some other way. For that purpose recourse was had, as described

TABLE III.—*Grain Sizes Given by Carburising and Ferrite-Precipitation Methods in Tests of 4 hr. at 1000° C.*

Sample No.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
	Carburised.	Ferrite Precipitation.
1	25	24
3, forged	45	45
6	804	796

below, to a surface effect produced in scaling which the author had studied some years ago.⁽⁴⁾

When steel is heated in air the boundaries of the surface grains become very resistant to attack by the usual acid reagents so that they stand out in strong relief on the etched surface. With Le Chatelier's cupric reagent the contrast produced is even more marked. A ready means is thus afforded of locating the austenite grains which existed immediately beneath the scale at the temperature of heating, and in order to compare the network structure thus revealed with that shown by ferrite precipitation it was merely necessary to bring the two into contiguity. There, however, a difficulty was encountered due to surface decarburisation. In the first attempts a narrow zone in which ferrite largely predominated separated the scaling network from that formed within the steel. Eventually it was found that a much closer juxtaposition could be obtained by covering a part of the ground surface to be scaled with a thick layer of a stiff paste made of finely ground alumina mixed with 6% of sodium carbonate and water. When the paste had dried the specimen was inserted in the furnace at 970° C., where it remained for 30 min. before being air-cooled. On detaching the scale there was usually a slight step downwards from the covered area. The raised portion was levelled and the surface then prepared on emery papers for examination. In that way a junction of one network with the other was effected, and, in the many specimens of different steels thus treated, the two were seen to be one and the same. At the dividing line no grain boundary was disclosed by scaling which was not also shown by ferrite precipitation. A typical example is given in Fig. 14; there the scaling network is white, while the ferrite network has been darkened by copper deposition.

Although it is convenient to describe the thin layers of the precipitated phase, whether they be ferrite or cementite, as grain boundaries, the term is not strictly correct, for in all probability the material in any one layer was provided by both the adjacent

grains, the original boundary being thus replaced by a band of new small crystals. In medium-carbon steel the granular formation of these marginal layers is but seldom brought out by ordinary etching methods, the narrow bands appearing to be continuous, especially in the case of cementite. It was found, however, that the grains in a ferrite network could be revealed by a very slow etching in a solution consisting of 95% alcohol containing 0.6 g. of picric acid per 100 c.c. A typical example is given in Fig. 15, which shows the tabular crystals in a ferrite network resembling that illustrated in Fig. 26. In applying the reagent the quantity taken has to be regulated to suit the size of the specimen so that the initial rate of attack soon slackens. Results similar to that shown in Fig. 15 were obtained in the following way: The specimen, weighing about 0.80 g., was placed slantwise with the prepared surface upwards in a crucible of 4 c.c. capacity, which was then filled with the reagent, covered and left undisturbed overnight. On removing the specimen the surface was cleaned by a light and repeated rubbing on a piece of moist Selvyt cloth until the structure was satisfactory under the microscope. A slight pitting occasionally took place, but it was chiefly confined to the edges.

This method of etching not only revealed the granular structure of the ferrite layers comprising the network but also the sub-boundaries within the pearlite areas, some of which are evident in Fig. 15. They are due to the fact that the transformation started at more than one point on the margins of the austenite grains, and as a result each pearlite grain contained several differently orientated areas. That mode of crystallisation occurs more frequently when the transition is fairly rapid, as was noted by Carpenter and Robertson⁽⁵⁾ in their study of the austenite-pearlite inversion.

SECTION 2, dealing with Grain Refinement and Growth in the Critical Range.

As is well known, eutectoid and hypo-eutectoid steels, even when coarsely crystalline, can be refined by heating them to a temperature just above that at which the last traces of ferrite disappear. Thus, whatever the initial grain size may be, growth in the austenitic range starts from a common basis of very small grains. Now, since no ferrite remains in a eutectoid steel when the A_{c1} transformation is ended, recrystallisation must take place entirely at that point, and hence it seems reasonable to infer that the areas of austenite which form at A_{c1} in a hypo-eutectoid steel are also refined, for these areas are not far from being eutectoid in composition. This conclusion was confirmed in the following way: Two specimens of a medium-carbon steel with a large grain size were heated to 750° C., whereupon one was quenched in water. The temperature of the furnace was then slowly lowered to 695° C., and as soon as that

was reached the other specimen was quenched. On examination, the original network of pro-eutectoid ferrite could still be seen in both specimens, but, whereas the areas of martensite in the 750° C. piece were almost unbroken, those in the 695° C. piece had been converted into many small islands, as shown in Fig. 16. Evidently, therefore, the austenite areas had been refined, and, although the new grain boundaries in the 750° C. specimen could not be discovered by etching, they were readily disclosed by the ferrite precipitation which took place as the temperature fell to 695° C. The failure to bring out the boundaries in the 750° C. piece was in all probability due to the fact that martensite embedded in ferrite strongly resists attack by etching reagents. This conversion of the pearlite areas at Ac_1 into a large number of smaller grains has previously been noted by Carpenter and Robertson,⁽⁶⁾ who state that "the areas of pearlite have a non-uniform appearance, because each has been formed from a number of grains of austenite."

Since austenite constitutes by far the greater part of a medium-carbon steel at the end of the Ac_1 transition, the refinement which occurs at that stage may be regarded as almost complete, for the grain size of the remaining pro-eutectoid ferrite cannot be large. It should be possible, therefore, for growth to begin before the steel has become entirely austenitic, and, in order to ascertain whether that actually happened, some tests were made near the upper limit of the critical range at temperatures which were thermostatically controlled to within $\pm 2^\circ$ C. For example, three specimens of sample No. 1 were heated together to 785° C. and after 1 hr. there one was withdrawn. The heating was then continued for a further 15 hr., when another specimen was withdrawn and, at the same time, the third was quenched in water so as to ensure that some ferrite was still present. This proved to be the case, for on examining the specimen narrow and widely separated bands containing residual ferrite were found, as shown in Fig. 17. Cupric etching indicated that these areas were situated along the most impure zones of the banded structure common to rolled steel as was to be expected, for the ferrite in such parts is always the last to disappear. Similar bands were also to be seen in the two air-cooled specimens, and between these zones in the 16-hr. piece a considerable amount of growth had taken place, as shown in Fig. 19. The finer structure of the specimen heated for 1 hr. is illustrated in Fig. 18. If the heating had been prolonged beyond 16 hr. the development would probably have proceeded still further, but the dimensions that any grain could ultimately reach would no doubt be limited by the distances apart of the ferrite zones, since these would act as barriers to growth.

When once all the ferrite was dissolved in the coarse-grained steels, the grain sizes already attained proceeded to enlarge without any structural hindrance. Thus the recrystallisation which began at the Ac_1 transformation was entirely confined to the critical range; in other words, the Ac_3 point was without significance and could be

ignored. This statement is based on evidence derived from two different experiments. In the first, the whole of the critical range was obtained in a single specimen, so that if a refinement occurred at the upper end of the range as well as the lower it should be apparent. Strips of the coarse-grained samples, 0.7 in. long, 0.2 in. wide and about 2.5 g. in weight, were used. They were inserted, one at a time, in the gradient half of the furnace up to $830^{\circ}\text{C}.$, and withdrawn after 7 min., during which period the centre of the furnace was maintained at $1000^{\circ}\text{C}.$, it having been found by preliminary quenching tests that under those conditions the Ac_1 point would travel about half-way along the strip. The position actually reached by the point was easily located by the sharp change from the as-rolled structure to that in which each pearlite area was composed of a set of new small grains, an illustration of which is given in Fig. 16. Then for a short distance onwards the original ferritic grain boundaries could still be traced, but beyond them no evidence of any additional refinement was to be seen.

In the second experiment, four specimens of the same steel were heated at $1050\text{--}1150^{\circ}\text{C}.$ in order to produce a fairly large grain size. The current was then switched off and one specimen withdrawn at about $1000^{\circ}\text{C}.$ At $725^{\circ}\text{C}.$ the current was switched on again and regulated so that the temperature fell to $710^{\circ}\text{C}.$, whereupon a second specimen was withdrawn, cooled at a moderate rate and slowly replaced along the gradient half of the furnace, the whole operation taking about 10 min. In the meantime the temperature had been maintained at $710^{\circ}\text{C}.$, and, as soon as the re-inserted specimen had attained that temperature, one of the two specimens which had been held at $710^{\circ}\text{C}.$ was water-quenched in order to ensure by examination that pearlite had not begun to form in the interval. Two specimens now remained in the furnace; their grain sizes were equal and pro-eutectoid ferrite was present in both, but they differed in that only one had passed through the Ar_1 transformation. Since the temperature was below the Ac_1 point this specimen was still pearlitic and consequently would be refined when the temperature was raised through the critical range. A comparison of these two specimens with that withdrawn at $1000^{\circ}\text{C}.$ would then show whether any recrystallisation occurred in the one held at $710^{\circ}\text{C}.$, which was, of course, the object of the experiment. The furnace was, therefore, slowly heated to $830^{\circ}\text{C}.$, and as soon as that temperature was reached the specimens were withdrawn.

This experiment was made on several of the samples, and in each instance the grain size of the specimen held at $710^{\circ}\text{C}.$ was identical with that of the one withdrawn at $1000^{\circ}\text{C}.$ A typical example is given in Figs. 20 and 21; the former shows the grain size produced in sample No. 6 at $1070^{\circ}\text{C}.$, the temperature of the initial treatment, while the latter shows the grain size in the $710^{\circ}\text{C}.$ specimen. Fig. 22 illustrates the refined structure of the specimen which was withdrawn at $710^{\circ}\text{C}.$ and replaced. The results obtained

by the counting method on three of the samples, including the above, are recorded in Table IV. They indicate conclusively that

TABLE IV.—*Absence of Refinement at the Upper End of the Critical Range.*

Sample No.	Initial Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
		Withdrawn at 1000° C.	Cooled to 710° C. only, then Heated to 830° C.
1	1½ hr. at 1100° C.	16	15
3	2 hr. at 1150° C.	17	16
6	1½ hr. at 1070° C.	18	18

the refinement in medium-carbon steels takes place for the most part during the Ac_1 transformation and that there is no further diminution in the grain size when the last of the ferrite disappears.

SECTION 3, *dealing with Grain Growth within the Completely Austenitic Range in Coarse-Grained Steels.*

The position has now been reached at which grain growth at temperatures above the critical range, the main subject of the paper, can be dealt with. As the investigation proceeded no less than eight interdependent factors were found to have a bearing on growth, and, since these had to be studied both separately and in combination, the task involved in a complete investigation became of such magnitude that it could be only partially attempted. Nevertheless, the number of tests, including duplicates, which were made ran to well over a thousand and was considered sufficient for a general survey. Every test was checked at least once and often several times. Confidence in the results was thus rapidly gained as the enquiry progressed, for under exactly the same conditions of treatment the same grain size began to be expected and was, in fact, obtained unless an effect to be described later as abnormal growth occurred. With that exception, nothing haphazard appeared in the formation of an austenitic grain size. Both the mode and the extent of growth seemed to be governed with remarkable consistency by the eight controlling factors, which were temperature, time, rate of heating, initial grain size, the aluminium content of the steel, hot-working, the rate of cooling to 1200° C. and the state of the carbide. They will be discussed in that order, and in the present Section the influence of the first three factors on growth in the as-rolled coarse-grained samples Nos. 1, 2 and 3 will be considered. The initial grain sizes of the samples are given in Table VIII., set B. Since the mode of growth in all three was very similar there will be no need to give a separate account of each.

Starting at a temperature immediately above that at which the last traces of ferrite vanished, the rate of growth in specimens held there was but little faster than that within the critical range. For instance, the grain size in a specimen of sample No. 1 when heated for 30 min. at 830° C. was not much larger than that seen in Fig. 18. The size attained in 7 hr. is reproduced in Fig. 23 and during 120 hr. in Fig. 24, which shows that even then many small grains remained. These three illustrations indicate the way in which growth

TABLE V.—*Increasing Rapidity of Growth with Temperature in Coarse-Grained Steels.*

Temperature. ° C.	Period during which Growth was Observed to Proceed. Hr.
850	24–36
930	8–10
1000	5–6
1100	2–3

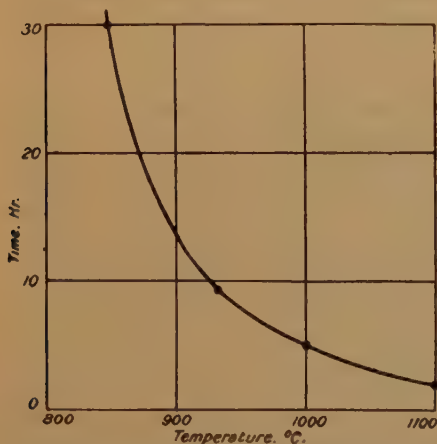


FIG. 1.—*Increasing Rapidity of Grain Growth with Temperature in Coarse-Grained Steels.*

shorter tests were carried out in order to ascertain the minimum time required to produce comparable structures. All three samples were examined in this way and the periods arrived at are covered by the intervals given in Table V. The curve in Fig. 1, which was obtained by plotting the average periods, affords a good idea of the acceleration of the rate of growth with increasing temperature.

At each of the temperatures stated in Table V. the mode of

took place. After a period of relative inactivity a number of the grains became singularly aggressive and began to absorb their neighbours. This process of dominant growth, as it will be termed, continued for a while steadily, but later the rate gradually diminished to zero, for the extent of growth in specimens heated at 830° C. for 48 hr. and 70 hr. was not perceptibly less than that observed after 120 hr. Evidently, therefore, a state of virtual stability had been reached. The same thing was found to occur at all temperatures up to at least 1100° C. in both coarse- and fine-grained steels, and use was made of it to assess approximately the speeding-up of growth as the temperature was raised. In so doing standards were first prepared by heating specimens for very long periods at four different temperatures, and then

growth was the same as at 830°C . After a period, the length of which was but a few minutes at 930°C . and barely observable at 1000°C ., certain grains became dominant. At first these grew fairly rapidly, but again the rate was not maintained, as is evident from the slope of the curves *A* and *B* in Fig. 2, where the average grain numbers within the standard area in specimens of sample No. 1 are plotted against the time of heating at 930° and 1000°C ., respectively. These tests did not altogether confirm the generally accepted view that the grain size of coarse-grained steels progressively enlarges as the temperature is raised above the critical range. It is true that when relatively short heatings were given the size could be said to increase gradually with the temperature, but when the heating was prolonged until a state of virtual stability was reached the grains at 1000°C . were no greater than some of those which developed most at 830°C . For instance, typical structures of sample No. 1 after 120 hr. at 830°C ., 72 hr. at 930°C . and 27 hr. at 1020°C . are shown, respectively, in Figs. 24, 25 and 26. At 930°C . fewer small grains remained than at 830°C ., while at 1020°C . the process of absorption by the dominant grains was practically completed, so that a fairly uniform network appeared; yet, as can be seen in the three illustrations, the largest grains were of about equal dimensions.

The attainment of a regular network at 1000°C . suggests that the most dominant of the multitudinous small grains formed in the critical range were approximately equi-spaced. It is by no means certain, however, that these grains retained their pre-eminence throughout, for, at a later stage, some of the lesser ones may have developed at the expense of their larger neighbours, as was observed by Carpenter and Elam⁽⁷⁾ in an interesting study of grain growth in a tin-antimony alloy. That the small grains in the samples now under consideration did not remain entirely stationary in size as dominant growth proceeded was quite evident. Whether as growth progressed one grain incorporated another bodily or by an insidious invasion could not be ascertained. In the investigation mentioned above the authors were able to demonstrate that the process was gradual and that one or more halts sometimes occurred in the outward movement of a boundary, but unfortunately the effect of which they made use is not exhibited by steel. Throughout the present enquiry only one thing was noticed which might have a

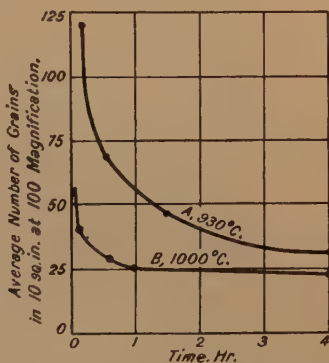


FIG. 2.—Rate of Grain Growth at (A) 930°C . and (B) 1000°C . in Sample No. 1.

bearing on this question. It consisted of a ferrite line which abruptly terminated before reaching the opposite side of a grain as though two grains were merging rapidly at the time of withdrawal from the furnace. An example is to be seen in one of the grains depicted in Fig. 28.

After dominant growth was completed at about 1000° C. the grain sizes in the samples began to enlarge as the temperature of heating was further increased, although the rate of growth was not rapid below 1200° C. Apparently at this stage a readjustment

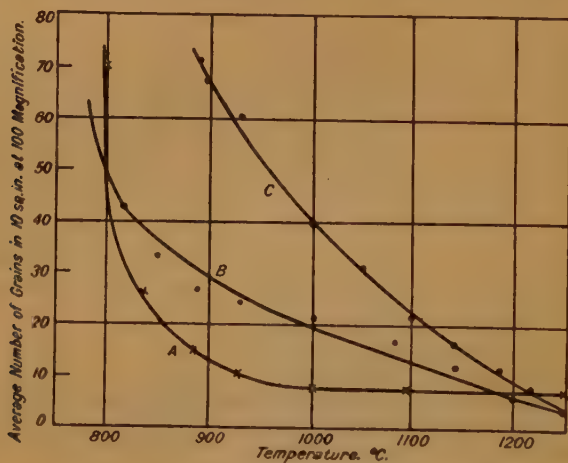


FIG. 3.—Grain Growth at Progressively Higher Temperatures in Sample No. 1. (A) Large initial grain size. (B) As-rolled, medium initial grain size. (C) Forged, small initial grain size.

of the grain boundaries took place in the manner described by Carpenter and Elam, for a fairly regular network was maintained. At temperatures up to about 1120° C. a state of virtual stability was eventually attained, but between 1150° and 1250° C., where several tests extending to 6 hr. were made, growth did not seem entirely to cease. The structure produced in sample No. 1 after 6 hr. at 1200° C. is shown in Fig. 28. At still higher temperatures the grain sizes quickly became very large, until at 1350° C. crystals of macroscopic dimensions were formed within half an hour. Curves B of Figs. 3 and 4 indicate the way in which growth progressed in samples Nos. 1 and 3 as the temperature was raised. In these graphs the average number of grains as determined by the counting method has been plotted against the temperature at which the specimen was held, the periods of heating being at least twice as long as those stated in Table V.

Thus far all specimens have been taken through the critical

range slowly, that is, at the rate of from 6° to 8° C. per min., as specified in Section 1. That grain sizes so obtained could be regarded as representative of slow heating in general was shown by tests in which four different rates ranging from 1° to 50° C. per min. were

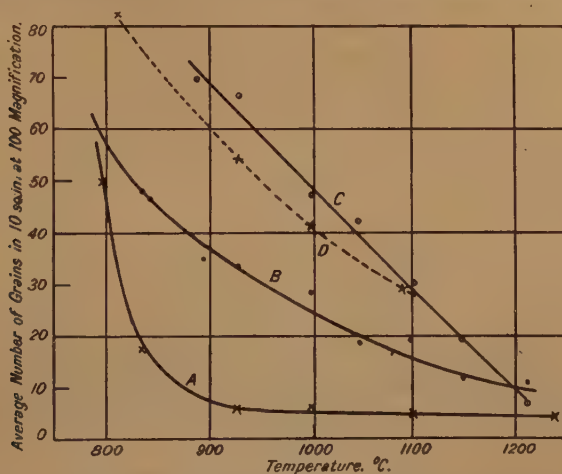


FIG. 4.—Grain Growth at Progressively Higher Temperatures in Sample No. 3. (A) Large initial grain size. (B) As-rolled, medium initial grain size. (C) Forged, small initial grain size. (D) Thermally refined, small grain size.

used. In each instance the specimen was heated to 1000° C. and held there for 7 hr. in order to ensure that a stable condition was reached. The results are given in Table VI.

TABLE VI.—Grain Sizes produced in Samples Nos. 1, 2 and 3 at 1000° C. after Various Slow Rates of Heating.

Sample No.	Temp. of Test. °C.	Average Number of Grains in 10 sq. in. at 100 Magnification. Average Rate of Heating per min.:			
		1° C.	8° C.	30° C.	50° C.
1	1000	22	21	23	22
2	"	32	32	31	33
3	"	29	29	30	30

As the speed of heating was increased beyond 50° C. per min. a diminution began to be noticeable in the fully developed grain sizes at temperatures below 1050° C. It was quite pronounced after a rapid heating and still more so when the rate had been very rapid. The extent of the reduction may be visualised from Figs. 25

and 27, which show respectively the structure of slowly and very rapidly heated specimens of sample No. 1 after they had been held for 72 hr. at 930° C. Further examples are presented in Table VII., in which are set out the grain sizes similarly produced in samples Nos. 1 and 2 at four temperatures between 850° and 1150° C. The

TABLE VII.—*Effects of Slow and Rapid Heatings on Grain Size in Coarse-Grained Steels.*

Sample No.	Temp. of Test. ° C.	Length of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
			Slow Heating.	Very Rapid Heating.
1	860	72	30	57
2	"	"	45	64
1	930	"	25	38
2	"	"	41	60
1	1000	27	22	37
2	"	"	32	52
1	1140	16	12	15
2	"	"	14	11

figures clearly indicate that the retarding effect of rapid heating on growth disappeared somewhere between 1000° and 1150° C. These results are in line with the observations made by Rosenberg and Digges,⁽⁸⁾ who found that the dominant factors controlling austenitic grain size in iron-carbon alloys of high purity were the rate of heating and the temperature.

While rapid heating considerably reduced the grain growth at temperatures below 1050° C., it did not affect the mode of development. As in slowly heated specimens, a number of the very small grains formed in the passage through the critical range became dominant and began to absorb the rest, until at about 1000° C. none but the dominant ones remained. This process usually led to the production of a uniform grain size, but not invariably, for sometimes an odd grain would outstrip its competitors and grow to outstandingly large dimensions. A striking example of this abnormal growth, as it will be termed, is shown in Fig. 29. Such predominance on the part of one or two grains was much less frequent in slowly heated than in rapidly heated specimens; in many instances the networks in the latter after they had been heated at between 1000° and 1050° C. were so irregular that no definite conclusion could be drawn from a comparison with the more uniform structures of the slowly heated specimens. Abnormal growth seemed to be very haphazard in character, for in repetitive work it might appear in one test and not in another.

The enlargement of one or more grains to dimensions well above the average has previously been noted by Carpenter and Robertson,⁽⁶⁾

who state that it arises when the steel "has previously been maintained for some time in the range of temperature where only certain grains grow," but they give no experimental evidence in support of this explanation. Several tests were therefore made in which specimens during a slow heating were kept for 2 hr. at temperatures between 830° and 870° C. before being held for 5 hr. at 1000° C. The results did not confirm the above suggestion, for in no instance was abnormal growth any more pronounced than when the heating to 1000° C. had been continuous. Even if abnormal growth had been thus facilitated the explanation would still be incomplete, since it fails to account for the marked increase observed in rapidly heated specimens.

Apart from the greater incidence of abnormal growth, grain development above 1000° C. in rapidly heated pieces followed much the same course as in those slowly heated. Between 1100° and 1150° C., however, abnormal growth became so frequent that, owing to the irregular grain sizes produced, it was difficult to ascertain whether a state of equilibrium could be reached. The indications were that above 1100° C. growth no longer came quite to a standstill. In slowly heated specimens abnormal growth was there more prevalent, and above 1200° C. differences due to the rate of heating entirely vanished.

SECTION 4, dealing with the Effect of Initial Grain Size on Growth in Coarse-Grained Steels.

That a relationship should exist between the initial grain size and the dimensions subsequently attained by the austenite grains might scarcely be anticipated, since all grain sizes are refined to an

TABLE VIII.—*Grain Sizes used in Tests on the Effect of Initial Size in Coarse-Grained Steels.*

Set.	Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.		
		Sample No. 1.	Sample No. 2.	Sample No. 3.
A	4 hr. at 1250–1300° C.	2	5	6
B	Billet, as-rolled	37	230	52
C	Forged billet and thermally refined billet	1300	1000	1500

approximately equal extent during the passage through the critical range. Nevertheless, in both coarse- and fine-grained steels the initial size was found to have a marked influence on growth at temperatures up to at least 1100° C. In examining the effect of this factor in the former class the grain sizes stated in Table VIII. were used.

The set *A* grain sizes were obtained by heating sections of the as-rolled samples for 4 hr. in a slab-reheating furnace, scaling and decarburisation being avoided by enclosing the pieces in a fireclay-coated mild-steel box, the corners and edges of which had been welded so as to make them gas-tight. For the production of the smallest sizes, both the mechanical and the thermal methods were employed, since it was not certain that growth would be the same in the two cases. To refine thermally, sections of the as-rolled samples were twice slowly heated to 850° C. for a few minutes and then furnace-cooled at the rate of about 10° C. per min. To refine mechanically, pieces from 2 in. to 3 in. thick were heated to approximately 1050° C. and forged down to flats $\frac{5}{16}$ in. thick under the steam hammer, care being taken to avoid any cold-working of the metal. As nearly as could be estimated the finishing temperature in each instance was about 800° C. In all three samples the grain sizes given by the two methods of refinement were very similar and resembled those illustrated in Figs. 34 and 35. Although the reduction by forging was considerable, one or two instances occurred where the disruption of some of the grains immediately below the surfaces was not complete, probably because the finishing temperature had been too high.* Such pieces were, of course, rejected, but they were nevertheless of interest in showing the degree of distortion of the original polygonal grains which took place before they were shattered. An example of the flattened but unbroken grains embedded in the fine grains of one piece is shown in Fig. 30.

When growth was examined in the very large-grained set *A* pieces, the periods required for the attainment of virtual stability at the several temperatures used in the tests were found to be about the same as those stated in Table V. for the as-rolled *B* pieces. After the refinement in the passage through the critical range dominant growth on the part of a very few grains became strikingly evident. Even at 820° C. a structure slowly appeared in which very large grains were mixed with groups of small ones, but at that temperature a standstill was reached before the latter were eliminated, for their number did not appreciably diminish when the heating was prolonged from 72 hr. to 120 hr. The extent of the growth in the set *A* piece of sample No. 3 after the 120-hr. treatment is illustrated in Fig. 31. As the temperature was raised the grain sizes which developed were much coarser than in the similarly treated set *B* pieces and yet the absorption of the small grains took place more readily. Their complete removal was effected at about 930° C., whereas in the set *B* pieces this required a temperature close upon 1000° C. Fig. 32 shows the grain size present in the set *A* piece of sample No. 1 after 27 hr. heating at 1000° C.; the smaller grain size formed at 1020° C. in the set *B* piece is illustrated in Fig. 26.

* In an interesting paper on the flow of metal, Massey demonstrates that during the forging of a flat bar the movement is greater at the centre than at the surface.⁽¹²⁾

Another difference observed in the behaviour of set *A* pieces was that from about 950° to 1250° C. no further growth of the dominant grains occurred. Within that temperature range the grain sizes obtained after prolonged heatings could be regarded as equally large, the only change being a gradual readjustment of boundaries in the direction of a more uniform network as the temperature approached the higher limit. This cessation of over-all growth is apparent in curves *A* of Figs. 3 and 4, where the grain sizes produced in samples Nos. 1 and 3 when virtual stability was reached have been plotted against the temperatures of the tests. The curves *B* in the graphs belong to the set *B* pieces.

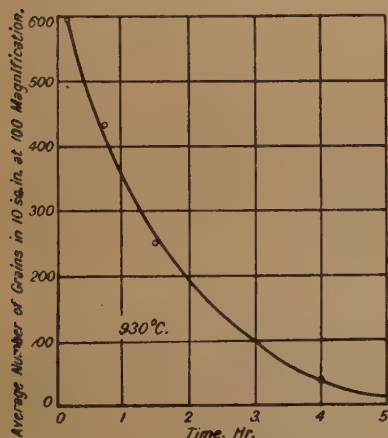


FIG. 5.—Rate of Grain Growth at 930° C. in Set *A* Piece of Sample No. 3, Table VIII.

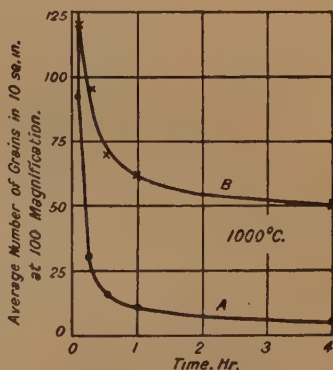


FIG. 6.—Rates of Grain Growth at 1000° C. in Pieces of Sample No. 3, Table VIII. (*A*) Set *A* piece. (*B*) Set *A* piece, forged.

Another feature of the set *A* pieces was that at stationary temperatures the time required for dominant growth to become unmistakably evident was considerably longer below 1000° C. than in the set *B* pieces. At 930° C. this period of slow progress lasted for at least 90 min.; yet after 4 hr. very few small grains remained, and, since their removal took a further 6 hr., it was obvious that, when once started, dominant growth must have proceeded fairly rapidly. The same feature was seen at 1000° C., except that the initial inactive stage was there comparatively short. Curves *A* in Figs. 5 and 6 show the decrease in the average number of grains in sample No. 3 during a period of 4 hr. at 930° and 1000° C., respectively. In passing, mention should be made of a structural effect which appeared in the 15-min. tests at 930° C. Dominant growth being but little advanced, many small grains were still present, and among them a coarse Widmanstätten structure could

be traced, as illustrated in Fig. 33. This pattern in greater or less distinctness was noticeable in most of the initially large-grained specimens of both coarse- and fine-grained steels after they had been heated for relatively short periods at temperatures below 950°C . Its occurrence implies that the previously existing orientations had not been altogether obliterated, but whether they remained in the set *A* pieces during longer periods at 930°C . could not be ascertained, owing to the increasing size of the dominant grains. Invariably, after a second short heating the pattern had entirely vanished, and for that reason sections were always heated through the critical range twice when refining thermally.

When specimens of the set *A* pieces were rapidly heated not only was the grain size reduced to a proportionately greater extent than in the set *B* pieces, but also the diminution persisted to a higher temperature. Moreover, the rate of heating could be appreciably slower before differences due to this variable entirely vanished. Some results obtained on the set *A* pieces of samples Nos. 2 and 3

TABLE IX.—*Effect of the Heating Rate on Growth in the Set A Pieces of Table VIII.*

Sample No.	Temp. of Test, $^{\circ}\text{C}$.	Period of Heating, Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification. Rate of Heating per min. :					
			1°C .	8°C .	35°C .	50°C .	400°C .	800°C .
2	1000	6	7	7	...	11	16	32
"	1100	"	...	8	17
"	1230	"	...	6	11
3	1000	"	5	6	9	20	37	70
"	1100	"	...	5	26
"	1230	"	...	4	12

are recorded in Table IX.; a comparison with those given by the set *B* pieces in Table VII. will show the greater sensitiveness of growth to the heating rate in the initially large-grained condition.

In dealing with the set *C* pieces, growth in the forged flats will first be described. As in the set *B* pieces, it was characterised by the early appearance of dominant grains, but their development was more restricted in that definitely smaller grain sizes were formed at temperatures up to at least 1100°C . When stability was reached, the grain sizes were practically identical in all three pieces and at 930°C . were similar to that shown in Fig. 37. The much larger grain size produced in the set *B* piece of the same sample at 930°C . is illustrated in Fig. 25. Dominant growth again progressed fairly rapidly in its early stages, but afterwards the absorption of the small grains proceeded very tardily, the rate being somewhat slower than in the set *B* pieces, notwithstanding that the grain sizes ultimately attained were less.

Another noticeable distinction was the more regular enlargement of the grain sizes as the temperature was raised to 1000°C . In the sets *A* and *B* pieces development below 1000°C was chiefly confined to the absorption of the small grains, as already stated, and while that continued the most dominant of the grains remained about equal in size. Typical examples of the rates of growth in the forged pieces at 930° and 1000°C are shown in Fig. 7, while the average grain sizes of samples Nos. 1 and 3 after prolonged heatings at temperatures between 850° and 1200°C are plotted respectively in curves *C* of Figs. 3 and 4. The curves *A* and *B* in the same graphs belong to the sets *A* and *B* pieces. Thus, over a wide temperature range the austenitic grain size was found to diminish as the initial size was reduced. The relationship was not linear, however, as can

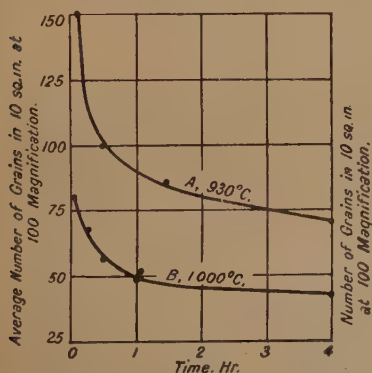


FIG. 7.—Rate of Grain Growth at (A) 930°C and (B) 1000°C in Sample No. 1, forged.

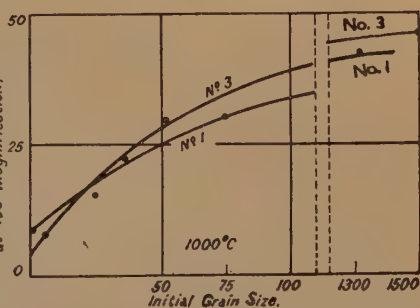


FIG. 8.—Diminution of Grain Size at 1000°C in Samples Nos. 1 and 3 as their initial grain sizes were reduced.

be seen in Fig. 8, where the grain sizes which developed at 1000°C in samples Nos. 1 and 3 have been plotted against the initial sizes.

In the tests on the forged pieces abnormal growth was encountered more frequently than in similar tests on either the set *A* or set *B* pieces, particularly at temperatures between 950° and 1050°C . Above 1050°C growth of that description became increasingly common and sometimes gave rise to very irregular structures. Occasionally a single grain would enlarge to a size far exceeding that of any other in the vicinity. An example which occurred in the forged piece of sample No. 3 when heated for 2 hr. at 1070°C is shown in Fig. 29. Now, since the average grain sizes produced at 1050°C were decidedly less than those given by the as-rolled set *B* samples, while at 1250°C no difference between them was observable, it is evident that within that temperature range the rate of growth prevailing in the forged pieces was the faster; in fact, this acceleration in the pace of development may account for the greater incidence of abnormal growth.

The effect of rapid heating on growth in the forged pieces was similar to that already noted in the sets *A* and *B* pieces. At temperatures up to 950°C ., the grain sizes were distinctly less than in the slowly heated specimens, as the three examples given in Table X. show. Above 950°C . abnormal growth happened so frequently that structures sufficiently uniform for a comparison were the exception. Nevertheless, the results in Tables VII., IX. and X., taken as a whole, clearly indicate that the restraining

TABLE X.—*Effect of Very Rapid Heating on Growth in the Set C Forged Pieces (Table VIII.).*

Sample No.	Temp. of Test. ° C.	Length of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification. Rate of Heating :	
			Slow.	Very Rapid.
3	870	68	70	89
1	900	72	68	88
1	1000	27	40	48

action on growth of a quick passage through the critical range became more pronounced and operated over a wider range of temperatures as the initial grain size was increased.

When growth in the thermally refined pieces was examined, the retarding influence of the initial grain size was again seen. In each instance a smaller size was formed at temperatures below 1050°C . than in the corresponding set *B* pieces, but the reduction was not so marked as in the forged pieces, as can be seen from the two examples given in Table XI. and also from curves *C* and *D* in

TABLE XI.—*Difference between Grain Sizes Produced in Forged and Thermally Refined Samples.*

Sample No.	Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.		
		As-Rolled.	Thermally Refined.	Forged.
1	68 hr. at 930°C .	25	38	61
2	" "	37	56	77

Fig. 4, curve *D* being that for the thermally refined piece. It was at first thought that the moderately large grains present before thermal refinement were still exerting an influence, notwithstanding the double treatment at 830°C ., but since the grain sizes produced at 930°C . were no smaller after the specimen had been heated four

times to 830° C., that explanation of the difference seemed improbable, although it could not be altogether discarded.

There was, however, another possible cause to be considered. The greater extent of growth after thermal refinement might be connected with the wide spacing of the banded structures in the pieces, for they had been taken from the as-rolled samples. In the forged flats the bands were, of course, much closer together. It was necessary to ascertain, therefore, whether the same disparity in growth still occurred in the absence of that variable, and for that purpose forged and thermally refined sections from two of the set *A* pieces were used, since they seemed to be quite homogeneous after their 4-hr. soaking at about 1300° C.

When etched with cupric reagents no heterogeneity appeared in them, nor could any be discovered after sections had been forged into flats. The homogeneity of the forged pieces was also indicated by the uniform distribution of the pearlite grains in specimens slowly cooled from 830° C. A typical example is given in Fig. 34, while the banding in a set *C* forged piece after a similar treatment is shown in Fig. 35.

When tests were made on the forged homogeneous pieces their austenitic grain development was found to follow the same course as in the corresponding heterogeneous samples. The rate of growth at 1000° C. in the set *A* piece of sample No. 3 is indicated by curve *B* in Fig. 6, and the average grain sizes attained in this sample at temperatures between 880° and 1250° C. are plotted in Fig. 9. That the removal of the banded structure caused no appreciable alteration in growth is obvious when the curve in Fig. 9 is compared with curve *C* in Fig. 4 for the forged heterogeneous piece. In the sections of the two set *A* pieces which were thermally refined grain development was also very similar to that in the corresponding heterogeneous samples, and at temperatures below 1000° C. they both gave a larger grain size than the forged pieces, as is shown by the results in Table XII. The structures produced during 48 hr. at 930° C. in the thermally refined and forged homogeneous pieces of sample No. 3 are illustrated respectively in Figs. 36 and 37.

These observations thus made it clear that the difference between the extents of growth in the forged and thermally refined conditions of the as-rolled samples were not connected with the spacing of the zones of heterogeneity. In fact, throughout the investigation no evidence appeared of any interference with growth by the normal banded structure except within the transition range, as was described

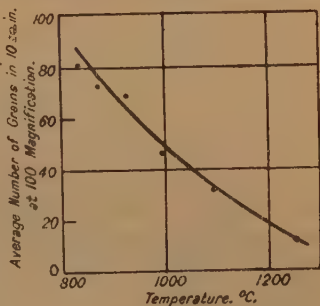


FIG. 9.—Grain Growth at Progressively Higher Temperatures in Set *A* Piece of Sample No. 3, forged, Table VIII.

in Section 2. As to the other possible explanation that the original grain size still had an influence on growth after thermal refinement, it should be noted that, although the initial grain size of the thermally refined set *A* pieces of sample No. 1 was much coarser than that of the set *B* piece, the latter gave a larger grain size at 930° C., as a comparison of the figures in Tables XI. and XII. will show. That

TABLE XII.—*Differences between Grain Sizes Produced in Forged and Thermally Refined Homogeneous Samples.*

Sample No.	Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
		Thermally Refined.	Forged.
1	68 hr. at 930° C.	44	72
3	" "	47	77

the behaviour of the thermally refined specimens could not be thus accounted for was also indicated after the refinement of a set *A* piece had been carried out in stages in order to reduce progressively the initial grain size. The successive treatments are stated in Table XIII. When a specimen from this piece and another from

TABLE XIII.—*Progressive Reduction of Grain Size in Repeated Heatings.*

Temp. of Heating. ° C.	Period of Heating.	Average Number of Grains in 10 sq. in. at 100 Magnification.
...	...	4
1100	1 hr.	...
1000	4 hr.	16
1000	4 hr.	32
920	6 hr.	55
860	2½ hr.	80
850	5 min.	...
840	5 min.	...
830	3 min.	1200

the forged homogeneous sample were heated for 48 hr. at 930° C. the same variation between the extents of growth in the two conditions was obtained. The results, together with those of a similar test at 960° C., are given in Table XIV.

Since these several experiments plainly showed that the divergence under discussion was due neither to heterogeneity nor to the grain size present before thermal refinement, the question as to whether hot-working itself was the cause began to be considered. If any energy absorbed by the steel during forging was retained

even partially when the austenitic range was again entered, the physical state would not be identical with that of the thermally refined section and consequently subsequent growth in the two might not follow the same course. But before hot-work could be regarded as a factor in growth there was still another difference between the mechanically and thermally refined pieces to be examined, which was that forging had changed the distances apart

TABLE XIV.—*Differences between Grain Sizes Produced in a Forged and a Thermally Refined Homogeneous Sample in which the Initial Grain Size had been Progressively Reduced.*

Sample No.	Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
		Thermally Refined.	Forged.
3	48 hr. at 930° C.	45	73
3	7 hr. at 960° C.	56	84

of the non-metallic inclusions along all three dimensions. Now, in order to ascertain whether this alteration had affected growth, it was necessary to eliminate, if possible, any hot-work in the forged pieces by heating them to a temperature above that used in forging but not high enough to disturb the inclusions. For this purpose a temperature between 1100° and 1150° C. appeared suitable, since the inclusions in the samples consisted of manganese sulphide and a relatively few silicates. Accordingly sections of the sets *C* and *A*

TABLE XV.—*Effect of Pretreatment at 1120° C. on Growth in Forged Samples.*

Sample No.	Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.		
		Forged.	Forged and 4 hr. at 1120° C., then Thermally Refined.	Thermally Refined.
1	68 hr. at 930° C.	62	44	38
3	“ “	76	56	50

forged pieces respectively of samples Nos. 1 and 3 were heated at 1120° C. for 4 hr. and afterwards cooled in the furnace. They were next doubly refined at 830° C., together with sections of the untreated forged pieces and also of the same samples in the unforged condition. Then, having ascertained that the grain sizes were equally small, specimens from all six sections were heated for 68 hr. at 930° C. The results are given in Table XV. Although

the distribution of the inclusions in the forged pieces which had received the preliminary soaking at 1120° C. had not been visibly changed, their grain sizes were now but little less than those of the thermally refined pieces. Hence, the relative positions of the inclusions had, at most, only a slight influence on growth, and there seemed to be no alternative to the conclusion that retained hot-work was the cause of the smaller grain sizes which developed in the forged pieces.

SECTION 5, *dealing with Growth in Fine-Grained Steels.*

Thus far the discussion of grain growth in the austenitic range has been confined to coarse-grained steels. This class will receive some further consideration later on and in the meantime the observations already made will provide a useful background for the study of growth in steels rendered fine-grained by the presence of aluminium, the next factor to be dealt with. As is well known, the addition of about 16 oz. per ton to a medium-carbon steel of good quality is sufficient to make it fine-grained. Since each new variable progressively increased the number of tests entailed in an examination of all the possible combinations, an extensive survey of growth in grades intermediate between coarse- and fine-grained was not attempted. It seemed better to pay most attention to steels which were shown to be thoroughly fine-grained by the McQuaid-Ehn test. The samples employed, *viz.*, Nos. 3D, 3E, 5, 6, 7 and 8 of Table I., were excellent examples of this quality, for, when tested in the as-rolled state by the above method, they each gave a No. 7 grain size even at 970° C. In fact, throughout the austenitic range their behaviour was very similar, so that illustrations taken from one will apply to all.

The first indication of the difference between the modes of growth in the two classes of steel appeared in tests on the as-rolled samples at temperatures within the critical range. It was noted earlier that a pronounced though slow grain enlargement could there take place in the coarse-grained type of steel, provided that the zones of heterogeneity containing the residual ferrite were widely separated, but, while this condition was also present in the fine-grained steels, no such development occurred. For instance, the fine-grain sizes which were formed in two specimens of the same sample when one was heated for 15 min. and the other for 48 hr. at 780° C. were almost identical. Even when the completely austenitic range was entered little, if any, general increase in grain size could be seen. Growth was again confined to the absorption of the most minute grains, and, except that, as was the case in the 48-hr. test at 780° C., a few gradually became incipiently dominant, the sizes remained very small. Typical examples are given in Figs. 38 and 39, which show respectively the grain sizes produced in specimens of sample No. 6 when heated for 5 min. and 18 hr. at

830° C. In the latter illustration the slight dominant growth mentioned above is evident, but this did not advance any further, for no change was perceptible after 144 hr. at that temperature. At 900° C. this dominant growth began within 5 min., yet there also it failed to continue. A check to further growth seemed to be in operation which, if not permanent, was at any rate very prolonged.

At 930° C. this state of inactivity still persisted for several days. Eventually, however, a very slow general growth could be detected and a day or two afterwards one or two large dominant grains appeared. In the case of sample No. 7 twelve days elapsed before growth approaching the extent shown in Fig. 42 was obtained; sample No. 6 required ten days and sample No. 5 six days. Thus an almost stationary condition intervened for a long period in the early stages of growth. This halt, as it will be termed, was the main distinguishing feature of the fine-grained steels. While it lasted the grain sizes remained small, although not equally so, for within narrow limits they could be varied by factors such as the initial grain size, but beyond that little more need be said about them.

As the temperature was raised above 930° C. the halt rapidly became shorter. At 960° C. unmistakable dominant growth began in approximately 24 hr., at 1000° C. in about 5 hr. and at 1100° C. within 15 min. When once this growth had started it continued until a condition of stability was reached exactly as in the coarse-grained steels, notwithstanding that the structures produced differed considerably, for in the fine-grained samples the small grains present during the halt remained almost unaltered in size until they were absorbed. The result was a lack of gradation as growth proceeded; very large grains developed in areas of comparatively small ones, thus giving rise to the so-called mixed grain sizes. An illustration is given in Fig. 41, which shows the structure of a specimen of sample No. 6 after it had been heated for 27 hr. at 1020° C. Other typical instances are to be seen in Figs. 58 and 66. The number of small grains in these mixed sizes diminished, of course, as the temperature was increased, but their removal was not completed below 1100° C. It should be remarked that invariably those at the periphery were the last to disappear and consequently the prepared surfaces of pieces which had been heated between 950° and 1050° C. were often bordered by a narrow zone consisting entirely of

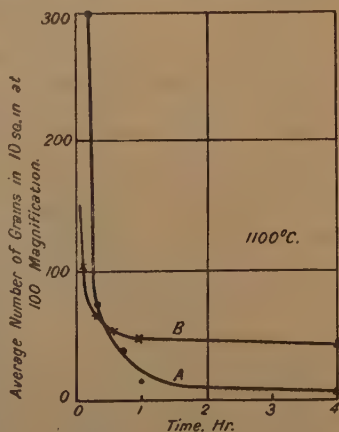


FIG. 10.—Rate of Grain Growth at 1100° C. in Sample No. 6.
(A) As-rolled. (B) Forged.

small grains, as illustrated, for example, in Fig. 78. As in the coarse-grained steels, the enlargement of the dominant grains was decidedly more rapid in the early stages of their development than later; at any rate that was the case at 1100°C. , as is shown by curve *A* in Fig. 10.

Another thing that distinguished growth in the fine-grained steels was the wavy contours of the dominant grains. In coarse-grained steels these grains were much smoother in outline and thus definitely polygonal. The only approach to uneven boundaries there encountered was in the tests below 950°C. on the set *A* pieces of Table VIII.; in fact, as shown in Fig. 31, the mixed grain sizes which formed in them while dominant growth continued strongly resembled those produced above 900°C. in the fine-grained samples. This similarity of growth also held after the small grains had been absorbed, for in both cases little, if any, further enlargement took place below 1250°C. Instead, the smaller grains began to encroach on their neighbours, with the result that the networks became more uniform as the temperature was raised. During this readjustment the grain boundaries also became straighter, so that eventually all distinction between fine-grained and coarse-grained steels disappeared. These changes are illustrated in Figs. 43 and 44, which show respectively the structures obtained in sample No. 6 when heated for 6 hr. at 1120° and at 1270°C.

A very striking feature of the mixed grain sizes which were in evidence while dominant growth proceeded was that in the subsequent air-cooling much less ferrite separated from the dominant grains than from the adjacent small ones, as can be seen, for example, in Fig. 42. Carpenter and Robertson⁽⁶⁾ have commented on this difference. They state that "the size of the austenitic grains affects the respective amounts of ferrite and pearlite formed during cooling," and, to quote again, "the first formation of ferrite occurs at the grain boundaries of the austenite. The smaller the grains the more boundaries there are in a given volume and therefore the more points at which ferrite may begin to form. This should not affect the amount of ferrite formed during cooling at the equilibrium rate, but under ordinary conditions of cooling, as in air, the number of points at which the formation of ferrite begins does affect the total amount formed." This explanation scarcely seems adequate, however, since it ignores the fact that ferrite may also be deposited on planes within the grains, as indeed readily occurs in lower-carbon steels even when the cooling is rapid. McBride, Herty and Mehl⁽⁹⁾ deduced from their experiments on ferrite separation in medium-carbon steels that the controlling factor was in all probability the rate of ferrite nucleation. This view is in many respects similar to that advanced by Carpenter and Robertson and may be correct, but it is rather surprising that ferrite nuclei should fail to appear within the grains while they form so rapidly at the boundaries. McBride and his collaborators affirm that at the latter position the induction period can be at most but a few seconds.

The ease with which ferrite is deposited at the grain boundaries was shown in an experiment made on a coarse-grained steel of nearly eutectoid composition containing carbon 0.78%, silicon 0.10% and manganese 0.62%. Two specimens were heated at 1200° C. for 30 min. in order to produce a large grain size; one was then withdrawn and the other slowly cooled in the furnace, a treatment which considerably increases the amount of pro-eutectoid ferrite in a medium-carbon steel. Yet, on examination, the two structures were found to be closely alike; in both instances a few short films of ferrite had been precipitated at the grain boundaries and, as far as could be judged, the quantities were about equal. Thus, although the short critical range had been traversed by the air-cooled specimen in less than 20 sec., as much ferrite had apparently formed in it as in the furnace-cooled specimen. From this and other similar tests the indications were that variations in the amounts of ferrite which separate from grains of different size in a specimen are confined to medium-carbon steels.

A rapid rate of heating influenced growth in the fine-grained steels in the same way as in the coarse-grained class but to a much greater degree, for, besides diminishing the grain sizes over a wider range of temperature, it caused a large contraction to take place in the extent and duration of the halt. In very rapidly heated specimens of samples Nos. 5 and 6 dominant growth began within 20 min. at 930° C., whereas after a slow heating a period of at least six days was needed. Thus, at a constant temperature the length of the halt could be greatly shortened, and to investigate this

TABLE XVI.—*Shortening of the Halt at 930° C. with Increasing Rates of Heating.*

Average Rate of Heating. ° C. per min.	Duration of Halt.
7	150 hr.
20	60 hr.
30	25 hr.
35	20 hr.
40	16 hr.
50	9 hr.
60	6½ hr.
200	3½ hr.
600	20 min.

variability further a series of tests was made at 930° C. on sample No. 6, in which the effects of intermediate heating rates were examined. With each rate used successively longer heatings were given until unmistakable dominant growth appeared similar to that shown in Fig. 59. The approximate halt periods so determined are stated in Table XVI., while in Fig. 11 they are plotted against the heating rates.

The acceleration of growth with an increasing rate of heating was further seen in a similar set of tests at 1000° C. on both samples

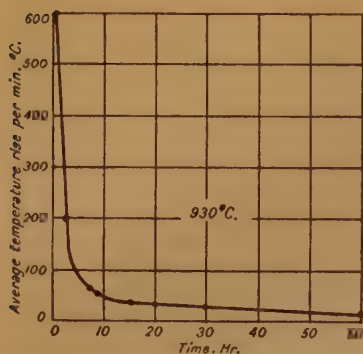


FIG. 11.—Length of the Halt at 930° C. in Sample No. 6 after different rates of heating.

Nos. 5 and 6. In this series the standard of comparison was an amount of dominant growth equal to that shown in Fig. 41, which typically represents the structure produced in a slowly heated specimen at 1000° C. when virtual stability had been reached. The results obtained on the two samples were in good agreement, and when plotted as in Fig. 12 they gave, as in the 930° C. tests, a curve which resembled a rectangular hyperbola. That rapid heating caused a large diminution of the halt was confirmed by the carburising test. Pieces of samples Nos. 6 and 7 were slowly raised to 1000° C. in

“ Hardenite ” contained in a fireclay tube. As soon as that temperature was recorded small specimens of the same samples, which had meanwhile been held at the cool end of the tube, were dropped into the mixture; the tube was quickly replaced and the heating

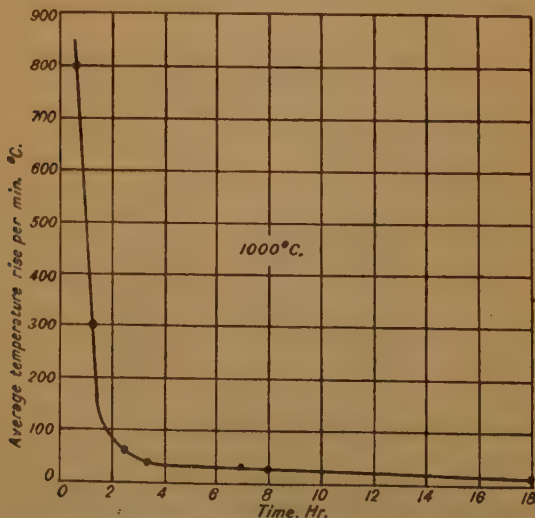


FIG. 12.—Periods Required to Attain Stability of Growth at 1000° C. in Sample No. 6 after different rates of heating.

continued for 2 hr. at 1000°C . On examination, the carburised areas of the slowly heated pieces were found to have a No. 7 A.S.T.M. grain size, there being no indication that dominant growth had started, whereas the very rapidly heated specimens had a No. 4 size.

Seeing that so wide a difference appeared between the lengths of the halts after slow and rapid heatings, an attempt was made by gradient-heating to produce a fine and a coarse structure in a single specimen. A bar of sample No. 5, 0.7 in. long, 0.2 in. wide and 2.5 g. in weight, was inserted in the gradient half of the furnace so that the front end stood at 760°C . Now, preliminary quenching tests had shown that when a specimen of the same dimensions was heated in that manner the Ac_1 point travelled about half-way down it in 8 min. After that period had elapsed, therefore, the tube containing the specimen was pushed into the uniform zone, which in the meantime had been maintained at 1000°C . Thus the critical range was entered at a fairly slow rate by the fore portion of the bar and traversed very rapidly by the remainder, so that by then heating the piece for 1 hr. at 1000°C . it was expected that dominant grain growth would occur only in the rapidly heated part. That was found to be the case, for after the above treatment the grain size of the back end of the bar was coarse while along the front portion it was entirely fine, the division between the two structures being quite sharp, as shown in Fig. 45. This experiment was repeated several times, and in each instance the same quick transition from a large to a small grain size appeared at some point along the bar.

The abruptness of the structural change in these specimens suggested that the rate of passage through the Ac_1 transformation was the governing factor in the duration of the halt rather than the rate of heating through the whole of the critical range. A closer examination was therefore made of the effect on growth of the speed at which the pearlite dissolved. In the first test, a 0.6-g. specimen of sample No. 5 was placed against a thermocouple which stood at 700°C . in the gradient half of the furnace and after about 15 min. the two were moved forward in steps of 0.5°C . per min. to 760°C ., at which temperature a little pro-eutectoid ferrite still remained. In order to increase the amount the specimen was then slowly drawn back to 715°C ., after which it was rapidly transferred to the zone at 1000°C . and held there for 1 hr., a period amply sufficient for a well-advanced dominant growth in a piece rapidly heated from below the Ac_1 point. But none occurred, the grain size being as small as that present during the halt in a slowly heated specimen, an example of which is given in one half of Fig. 45. The above test was then repeated except that this time the specimen was rapidly heated from 720°C ., a temperature just below the Ac_1 point. A large grain size was now produced similar to that shown in the other half of Fig. 45. Finally, a third test was made in which the same procedure was again followed, but in this instance

the specimen was slowly moved along the furnace from 700° to between 735° and 740° C. and held there for a few minutes, preliminary tests having shown that by so doing about one-half of the pearlite would be dissolved. In this specimen a mixed grain size was formed resembling that illustrated in Fig. 42, and, from the results of the previous tests, there could be little doubt that the large dominant grains existed in areas where the solution of the greater proportion of the pearlite had been rapid.

The conclusion was thus drawn that the speed of the pearlite transformation was the chief cause of the wide variation in the lengths of the halts in specimens heated at different rates. Subsequently, a possible reason for this was discovered when examining two 0.8-g. specimens which had been inserted in the furnace at 1000° C. and quenched, as it happened, while the Ac_1 transformation was in progress. In both instances the undissolved pearlite was found to be entirely lamellar and seemingly unaltered, whereas it had repeatedly been observed that in similarly quenched slowly heated specimens the residual cementite laminae were largely broken up into extremely fine particles. The two formations are illustrated respectively in Figs. 46 and 47. Apparently, therefore, pearlite in process of solution becomes increasingly spheroidised as the speed of the Ac_1 change is reduced, and, since, as will be shown later, dominant grain growth was on a smaller scale after a complete spheroidisation into comparatively large particles, it may be that an approach to this condition was the cause of the lengthening of the halt as the rate of heating was lowered.

Having found a connection between the rapidity of the Ac_1 transformation and the duration of the halt, the question now remained as to whether any additional influence was exerted by the rate at which the rest of the critical range was traversed. For that part of the enquiry it was necessary to ascertain the effects on the halt of a slow solution of the pearlite followed by a rapid heating and *vice versa*. The first of these two treatments presented no difficulty and has already been described. Specimens of samples Nos. 5 and 6 were slowly heated, one at a time, to 760° C. along the gradient half of the furnace and then brought back in a few minutes to 715° C., after which they were transferred to the zone at 1000° C. and held there for 2½ hr. The results were not very conclusive, but, on the whole, they seemed to indicate that the halt was shortened a little, for more than once dominant growth had passed the incipient stage. Usually it took 4 hr. for that to occur when specimens of the above samples were slowly heated through the whole of the critical range, although very occasionally an odd dominant grain appeared in the 3-hr. tests at 1000° C.

Unfortunately, the converse experiment was not practicable. The only course open was to heat the specimen rapidly to about 970° C. and then, without any delay, to lower the temperature to 715° C. so that the required slow upward passage through the re-

mainder of the critical range could be given. It was considered that this second entry into the critical range was permissible, since previous tests had shown that when once the Ac_1 point had been passed no further general refinement took place as the steel became completely austenitic. This particular experiment received a great deal of attention and was made repeatedly on all the fine-grained samples. As a rule four specimens were used in the manner set out in Table XVII. Nos. 1, 2 and 4 each weighed about 0.8 g., No. 1 being the actual test specimen. No. 2 was withdrawn at 900° C. in order

TABLE XVII.—*Log of a Test on Rapid Heating through Ac_1 Followed by Slow Heating to 1000° C.*

Time.	Temperature of Furnace. ° C.	Procedure.
10.00 A.M.	970	Nos. 1, 2 and 3 specimens inserted;
10.03 A.M.	"	current switched off.
10.08 A.M.	900	No. 2 specimen withdrawn;
10.25 A.M.	725	current switched on.
10.40 A.M.	705	No. 3 specimen quenched in water; current increased.
11.20 A.M.	830	...
11.30 A.M.	970	No. 4 specimen inserted.
11.35 A.M.	1000	...
12.35 P.M.	1000	Nos. 1 and 4 specimens withdrawn.

to make reasonably certain that dominant growth had not started in No. 1. No. 3, quenched from 705° C., served as a check on the pyrometric reading, for it was essential that no pearlite should form in No. 1. No. 4 was included so that the structure of No. 1 could be compared with that produced after a rapid heating through the whole of the critical range. As a result of the numerous experiments carried out in this way it was found that the halt was lengthened a little by the slow passage through the critical range above the Ac_1 point. To obtain a dominant grain growth in specimen No. 1 equal to that in specimen No. 4 at 1000° C. a temperature of about 1015° C. was needed. This retardation could be regarded as slight when set against the long halt which followed a slow heating from below Ac_1 , so that the rate of heating above the critical point was again seen to be of minor importance.

Since the initiation of dominant growth in fine-grained steels had been found to take a progressively longer time as the rate of passage through the critical range was reduced, it seemed desirable to examine more closely the very early stage of growth in coarse-grained steels, in order to ascertain whether any indication of a similar effect appeared in them, for in that case the difference between the two classes could be regarded as merely one of degree. The tests were made in the following way: Two 0.25-g. specimens of a sample were each fastened to a length of thin wire and along this a holder of

fine silica tubing was firmly fixed against the specimen. The two specimens were then placed in the gradient half of the furnace at about 680° C., and after a short while one of them, together with the thermocouple, was slowly moved forward in steps of 0.5° C. per min. until 790° C. was recorded, whereupon both specimens were rapidly pushed into the uniform zone, which had previously been set at 930° C., where they remained for exactly 2 min. before withdrawal for examination. It was observed that the 790° C. specimen took about 10 sec. to reach 930° C., while the 680° C. specimen required approximately 25 sec.; yet, in all the tests, growth in the latter was the more advanced. Typical examples showing the difference are given in Figs. 48 and 49, which illustrate respectively the grain

TABLE XVIII.—*Grain Sizes Produced at 1120° C. in Sample No. 6 after Different Rates of Heating.*

Approximate Heating Rate. ° C. per min.	Period of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification.
7	2	9
25	"	12
70	"	15
350	"	35
500	"	51
800	"	65
1000	"	75

sizes in the 790° and 680° C. specimens of sample No. 1. Thus slow heating caused a slight but definite retardation of growth in the initial stage of development even in coarse-grained steels, and it may be that an aluminium addition accentuates this effect to such an extent as to occasion a long halt whereby the steel becomes fine-grained in character.

Besides shortening the halt, a rapid heating of the fine-grained

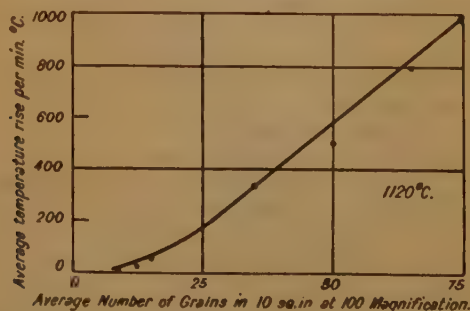


FIG. 13.—Diminiution of Grain Size at 1120° C. in Sample No. 6 with increasing rates of heating.

samples also reduced noticeably the small grain sizes present during that period, while after dominant growth had occurred the diminution in grain size was very striking, being more pronounced than in coarse-grained steels and persisting to a higher temperature. Fig. 50, for instance, shows the structure of a rapidly heated specimen of sample No. 6 after 6 hr. at $1120^{\circ}\text{C}.$; the much larger grain size of the same sample when slowly heated is illustrated in Fig. 43. So sensitive was growth in the fine-grained steels to the speed of heating that even when the rate was as low as $25^{\circ}\text{C. per min.}$ the grain sizes formed at 1120°C. were appreciably smaller than in slowly heated specimens. An example of the progressive lessening of the grain sizes which were obtained in sample No. 6 at the above temperature as the rate of heating was increased is given in Table XVIII.; the figures are plotted in Fig. 13.

Another marked effect of an acceleration in the rate of heating was the gradual lowering of the temperature at which dominant growth could be completed. Very few small grains remained in

TABLE XIX.—*Grain Sizes in Very Rapidly Heated Specimens of Sample No. 6.*

Temp. of Test. $^{\circ}\text{C.}$	Period of Heating.	Average Number of Grains in 10 sq. in. at 100 Magnification.
930	5 days	68
1020	2 "	57
1120	$4\frac{1}{2}$ hr.	75
1220	$4\frac{1}{2}$ "	39
1270	6 "	5

very rapidly heated specimens after they had been held for five days at 930°C. , whereas in slowly heated pieces an equal elimination was never seen at temperatures below 1100°C. Grain size determinations could thus be made over a much wider temperature range than when the rate of heating was slow. Some typical results are presented in Table XIX. As there shown, the smallest size was produced at about 1120°C. ; at 930° and 1020°C. the dominant grains, though relatively small, were definitely larger, no doubt because the rate of heating was necessarily less rapid. As the temperature was raised above 1150°C. the grain sizes began to enlarge, so that they steadily approached those formed after a slow heating until at about 1300°C. all distinction vanished. Parity was reached by the abnormal growth of a few grains, as was the case in the coarse-grained steels.

When the initial grain size was examined as a factor in austenitic grain development, it also was found to have a greater influence than in coarse-grained steels. Comparisons were again made between growth in the samples as-rolled and in sections which had been refined both thermally and mechanically. The latter operation was carried out in the manner described in Section 3, while in the

thermal treatment the pieces were twice heated to 930°C . and then furnace-cooled. The grain sizes produced by both methods were very small and approximately alike, their number being about 2000 per sq. in. under the standard magnification adopted for the determination.

On heating specimens of refined pieces to a temperature not exceeding 850°C . the extremely small grain sizes which resulted from the passage through the critical range remained almost unaltered for an indefinite period, and invariably they were appreciably less than those given by the as-rolled samples. Fig. 40, for example, shows the structure of a thermally refined piece of sample No. 6 after it had been heated for seven days at 830°C .; that of the as-rolled sample after 18 hr. at the same temperature is seen in Fig. 39. Similar differences appeared at 930°C ., provided that the period of heating was not more than 2 hr. It was thus clear that to obtain a full advantage of the halt in growth for the refinement of fine-grained steels with a large grain size a double heating at least should be given. The need for this was also indicated by the fact that, as in coarse-grained steels, a single heating seldom sufficed to obliterate entirely the Widmannstätten structure of the original grains; in some of the samples it was remarkably distinct.

The degree of refinement attainable by repeated heatings was found to be limited, however, for when sections of the as-rolled samples were heated four times for 30 min. at 830°C . and air-cooled after the final heating no further diminution of grain size was noticeable. It should be remarked in passing that the small grains produced by thermal refinement did not increase in size when the pieces were slowly cooled. If anything, the greater separation of ferrite as crystals caused a slight diminution except where banded zones of heterogeneity appeared. In such areas the ferrite grains became definitely larger. An example is given in Fig. 51, which shows a ferritic band in a forged piece of sample No. 6 after it had been heated twice to 930° and then once to 830°C ., followed by a gradual cooling in 5 hr. to 650°C . Fig. 52 illustrates the more uniform grain size in a similarly treated section which had first been heated for 2 hr. at 1250°C . in order to remove the banded structure.

Above 850°C . the halt in the refined pieces became much shorter than that in the as-rolled samples. In the latter dominant growth began in six to ten days at 930°C . and in 4–5 hr. at 1000°C ., whereas after refinement the respective periods at these temperatures were $3\frac{1}{2}$ –5 hr. and not more than 10 min. Nevertheless, subsequent development proceeded in the same manner as in the as-rolled samples. Towards the end of the halt there was a slight general enlargement of the grains, until eventually a few became dominant; these then continued to absorb the small grains, and the mixed sizes thus formed were not entirely removed at temperatures below 1100°C . But although this mode of growth resembled that in the as-rolled samples, the resulting grain sizes were considerably less.

For instance, the grain size of the forged piece of sample No. 6 after 6 hr. at 1120° C. shown in Fig. 53 is very much smaller than that of the similarly treated as-rolled section seen in Fig. 43. A comparison of the figures for slow heating in the 1100° and 1150° C. tests given in Table XX. will also indicate the extent of the difference.

TABLE XX.—*Extent of Grain Growth in Sample No. 6, As-Rolled and Forged.*

Condition.	Initial Grain Size.	Rate of Heating.	Length of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification. Temp. of Heating:				
				1100° C.	1150° C.	1220° C.	1270° C.	1350° C.
As-rolled	16	Slow	2-6	9	5	5	4	2.5
"	16	Very rapid	"	65	75	39	5	...
Forged	2000	Slow	"	45	43	26	12	2.0
"	2000	Very rapid	"	150	160	...	10	...

Notwithstanding the smaller grain size produced, the speed of growth in the refined pieces at 1100° C. was no faster than in the as-rolled samples. That is evident in Fig. 10, where curves *A* and *B* show the progress of growth at the above temperature in the as-rolled and forged conditions, respectively, of sample No. 6. Between 1150° and 1270° C. the grain boundaries straightened out, as was the case in the as-rolled samples; yet, even after 6 hr. at 1270° C. equality in size was not reached. Occasionally within that temperature range the abnormal growth of one or two grains occurred; above 1270° C. it became increasingly common, until at 1350° C. variations due to initial grain size were entirely eliminated in less than 30 min.

A rapid heating of the refined pieces caused a further big contraction both of the temperature range and of the duration of the halt. At 930° C. this period of inactivity lasted but a few minutes and at 1000° C. it could not be detected. Moreover, subsequent growth was so restricted that mixed grain sizes of the kind illustrated in Fig. 58 did not appear even when the rate of heating was only moderately rapid. The extent of the reduction in the forged piece of sample No. 6 is indicated in Table XX. Fig. 54 shows a typical area in a specimen of that sample which had been very rapidly heated to 1120° C. and held there for 6 hr. A comparison with Fig. 43, which shows the structure produced in the slowly heated as-rolled sample at 1120° C., will illustrate the wide range of stable post-halt grain sizes that was obtained in any one sample at a constant temperature simply by changing the rate of heating and the initial grain size. As determined by the counting method, the figures for the two grain sizes depicted in Figs. 43 and 54 were 5 and 150, respectively. Expressed in another way, the number of grains per cubic inch

was approximately three hundred and fifty thousand in the slowly heated as-rolled sample after 6 hr. at 1120° C. and fifty-eight million in the forged piece. Although a very rapid heating of the refined samples caused the smallest post-halt grain size of any to form between 1100° and 1150° C., the degree of diminution was not so great as when the initial grain sizes were larger; in other words, the effect of rapid heating became more marked as the initial grain size was increased. This feature is exemplified by the results in Table XXI., where it will be seen that the ratios of the very-rapid-

TABLE XXI.—*More Pronounced Reduction of Grain Size due to Rapid Heating as the Initial Grain Size was Increased.*

Sample No.	Initial Grain Size.	Temp. of Test. ° C.	Period of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification. Rate of Heating :		Ratio.
				Very Rapid.	Slow.	
6	16	1100	3	65	9	7.3
6	49	"	"	86	20	4.3
6	2000	"	"	150	45	3.3
7	4	"	"	74	7	10.6
7	136	"	"	88	36	2.4
7	900	"	"	102	56	1.8

heating to the slow-heating grain sizes in the last column decrease with the initial grain size.

It was stated in Section 3 that slowly heated forged pieces of the coarse-grained steels developed a smaller grain size than the thermally refined pieces at temperatures up to about 1050° C. A similar difference was also observed within that range in fine-grained steels, especially after specimens had been rapidly heated, probably

TABLE XXII.—*Effect of Hot-Work on Grain Size after Rapid Heating.*

Sample No.	Rate of Heating.	Temperature of Test. ° C.	Period of Heating. Hr.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
				Forged.	Thermally Refined.
6	Very rapid	1030	7	182	128
7	Rapid	"	"	135	87

because a fairly complete dominant grain growth was then obtained. Two examples are recorded in Table XXII. In specimens slowly heated to temperatures not exceeding 1050° C. mixed grain sizes were formed, and, in them, too, the dominant grains were definitely

larger after thermal refinement, but when the smaller grains were eliminated by heating at 1120°C . the disparity was barely noticeable. That by no means contradicted the view already expressed that the hot-working of the forged pieces was the cause of the variation, for tests on the coarse-grained samples indicated that at 1120°C . most of the retained hot-work was removed.

In examining growth in samples representing the transition stages between coarse- and fine-grained steels, attention was chiefly given to the effect of a progressive increase in the aluminium content on the temperature range and duration of the halt. Most of the tests were made on the No. 3 group of samples in Table I., which were taken from the billets rolled from six successive 3-ton ingots of the same cast to which quantities of aluminium ranging from nil to 32 oz. per ton had been added gradually as the moulds were being filled. These billets had, of course, a fairly large grain size, and a second set of pieces with a much smaller size was therefore prepared by forging a portion of each billet to a 1-in.-square bar, care being exercised that the finishing temperature was about 800°C . Besides these samples several others were also used of both acid and basic qualities with ladle additions of from 1 oz. to 9 oz. of aluminium per ton. Further reference to them is, however, unnecessary, since in every instance the manner of the grain development was similar to that in the corresponding member of the No. 3 series.

The way in which the normal mode of growth in coarse-grained steels changed into that characteristic of fine-grained steels was well seen in a test carried out on the forged pieces of the No. 3 samples specimens of which were heated together for 45 min. at 960°C . The structures produced are shown in Figs. 56 to 60 in the order of increasing aluminium content. In the specimens containing no aluminium and 1 oz. per ton the grain sizes could not be distinguished, and as that was also the case in a 10-min. test at 930°C . there was no need to include an example of the No. 3A grain size in the above set of illustrations. The presence of 3 oz. per ton of aluminium caused a rather mixed grain size to form, in which dominant grains largely preponderated; with 9 oz. per ton the grain size was very mixed, but dominant growth was not so far advanced. It was still less so in the specimen with 16 oz. per ton, while in that with 32 oz. per ton the halt had not been passed, for the grain size was entirely small. A similar mode of transition was described some years ago by Hertý, McBride and Hollenback,⁽¹⁰⁾ their examples being obtained from four different casts to which aluminium additions ranging from 8 oz. to 24 oz. per ton had been made.

The same progressive retardation in growth was apparent when the above test was applied to the as-rolled samples, although the development of the dominant grains in the intermediate samples did not proceed as far as in the forged pieces, owing to the restraining influence of the much larger initial grain sizes. The structure

of the 3-oz. per ton specimen now resembled that shown in Fig. 58; in the 9-oz. per ton specimen dominant growth had barely started, while in the 16-oz. and 32-oz. per ton specimens the grain sizes were equally fine. Once more no variation was observable between the extents of growth in the specimens containing no aluminium and 1 oz. per ton. It was thus evident that, when other factors were kept constant, the halt was lengthened as the aluminium addition was increased beyond the amount required for the initiation of the change, and this inference was fully supported by further tests in which specimens of the six samples were heated for prolonged periods at temperatures below 960°C . Some of the results, including those described above, are summarised in Table XXIII.

TABLE XXIII.—*Changes in Grain Growth with Increasing Aluminium Content.*

Condition of Sample.	Temperature of Test, $^{\circ}\text{C}$.	Length of Heating.	Sample No. and Aluminium added per Ton.					
			3. Nil.	3A. 1 oz.	3B. 3 oz.	3C. 9 oz.	3D. 16 oz.	3E. 32 oz.
Forged	960	30 min.	Coarse	Coarse	Mixed	Mixed	Growth started	Fine
As-rolled	"	30 "	Coarse	Coarse	Growth started	Incipient growth	Fine	Fine
"	850	92 hr.	Coarse	Coarse	Growth started	Fine	Fine	Fine
"	880	72 "	Coarse	Coarse	Mixed	Fine	Fine	Fine
"	930	67 "	Coarse	Coarse	Mixed	Fine	Fine	Fine

Another point should here be mentioned. In all these tests the transition from the coarse-grained structures given by samples Nos. 3 and 3A to a wholly fine-grained structure proceeded in the manner shown in Figs. 56 to 60. A gradual reduction of the grain sizes did not occur; those formed in the intermediate samples were either coarse or fine or else mixed. It would seem, therefore, that the control of grain size at ordinary heat-treatment temperatures by means of aluminium additions is limited to the production of the small sizes present during the halt. To obtain sizes nearer to those given by coarse-grained steels a regulated dominant growth is needed, and the use of aluminium then offers little, if any, advantage, since but a few ounces per ton may raise considerably the temperature at which complete dominant growth can take place. A further complication is that the post-halt grain sizes become larger as the aluminium content is increased, as was first noticed by Grossmann,⁽¹¹⁾ who described this growth as exaggerated. An example was provided by the No. 3 samples in the as-rolled condition, the grain sizes of which are given in Table XXIV. The same effect was seen in a test on four of the samples after they had been doubly refined at 850°C ., for when the specimens were heated for 4 hr. at 1130°C ., so as to get full growth in all, a progressive expansion of the grain

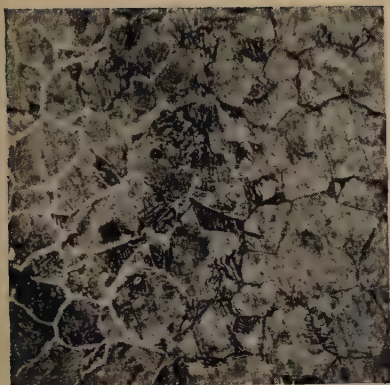


FIG. 14.—Scaling and Ferritic Grain Boundaries. Cupric etch. $\times 90$.

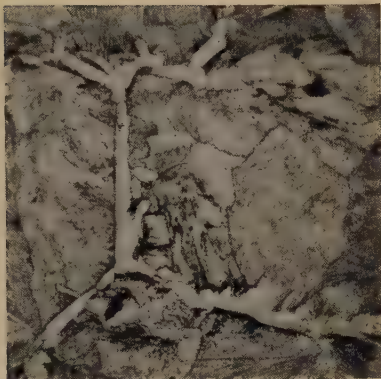


FIG. 15.—Ferrite at Grain Boundaries. Very slow etch. $\times 450$.

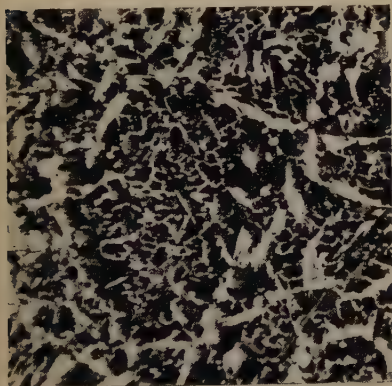


FIG. 16.—Sample No. 1, heated to 750°C ., quenched from 695°C ., slightly tempered. $\times 95$.

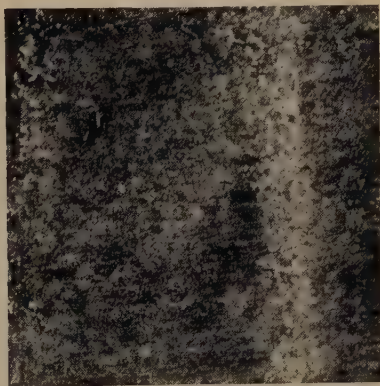


FIG. 17.—Sample No. 1, 16 hr. at 785°C ., quenched, slightly tempered. $\times 55$.

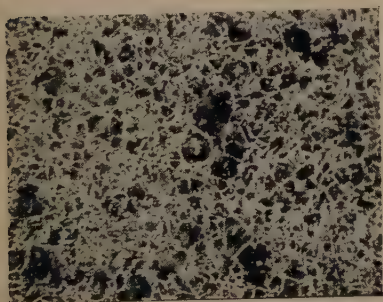


FIG. 18.—Sample No. 1, 1 hr. at 785°C ., air-cooled. $\times 55$.

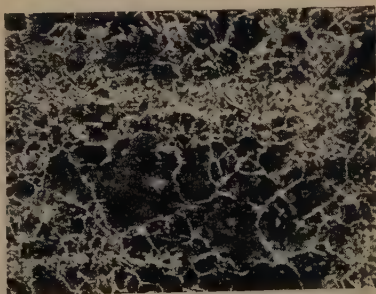


FIG. 19.—Sample No. 1, 16 hr. at 785°C ., air-cooled. $\times 55$.

[Whiteley.
To face p. 552 P.]

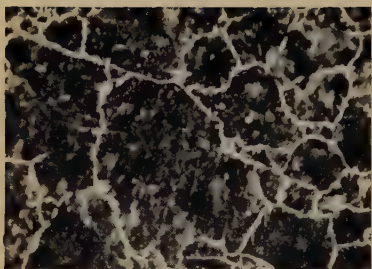


FIG. 20.—Sample No. 6, $1\frac{1}{2}$ hr. at 1070°C . $\times 55$.

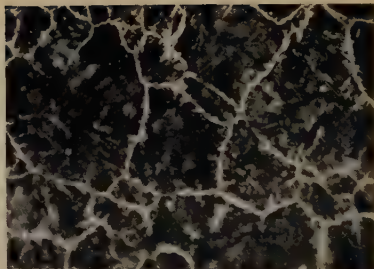


FIG. 21.—Sample No. 6, $1\frac{1}{2}$ hr. at 1070°C ., cooled to 710°C ., heated to 830°C . $\times 55$.

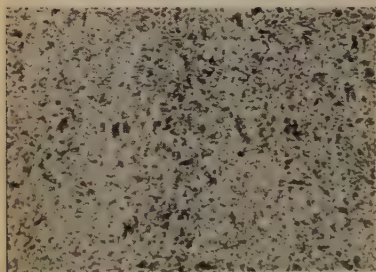


FIG. 22.—Sample No. 6, $1\frac{1}{2}$ hr. at 1070°C ., cooled to 20°C ., heated to 830°C . $\times 55$.

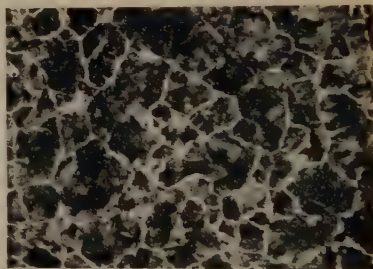


FIG. 23.—Sample No. 1, 7 hr. at 830°C . $\times 55$.

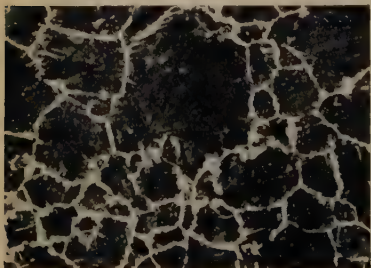


FIG. 24.—Sample No. 1, 120 hr. at 830°C . $\times 55$.

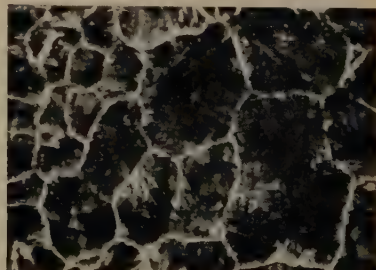


FIG. 25.—Sample No. 1, 72 hr. at 930°C . $\times 55$.

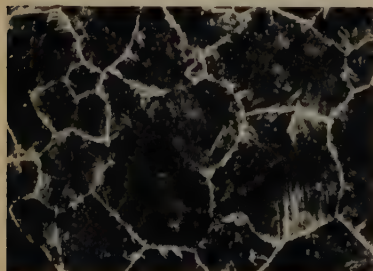


FIG. 26.—Sample No. 1, 27 hr. at 1020°C . $\times 55$.

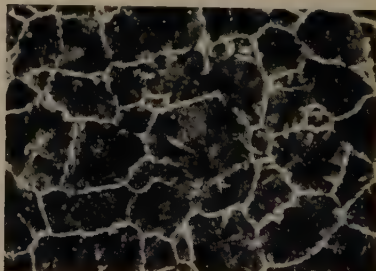


FIG. 27.—Sample No. 1, rapidly heated, 72 hr. at 930°C . $\times 55$.

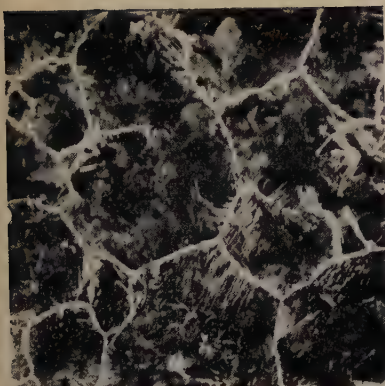


FIG. 28.—Sample No. 1, 6 hr. at 1200° C. $\times 55$.

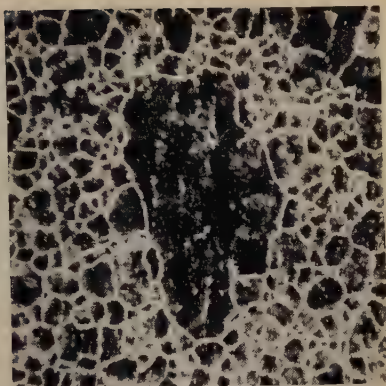


FIG. 29.—Sample No. 3, forged, 2 hr. at 1070° C.
Abnormal growth. $\times 18$.

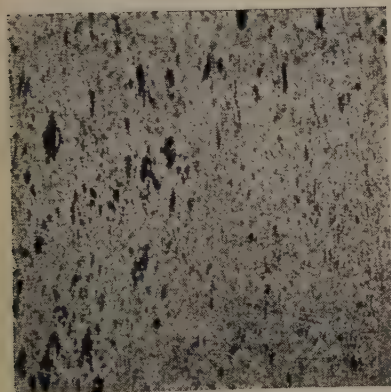


FIG. 30.—Sample No. 5, forged, near surface.
 $\times 25$.

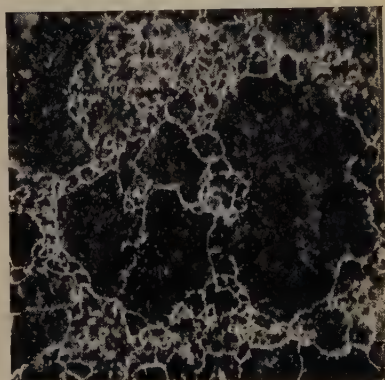


FIG. 31.—Sample No. 3, set A piece, Table VIII.,
120 hr. at 820° C. $\times 25$.

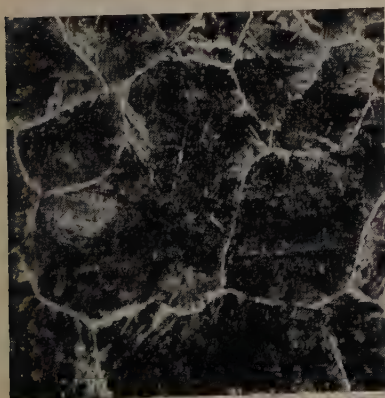


FIG. 32.—Sample No. 1, set A piece, Table VIII.,
27 hr. at 1000° C. $\times 55$.

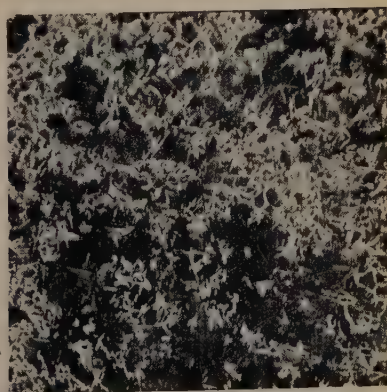


FIG. 33.—Sample No. 3, set A piece, Table VIII.,
15 min. at 930° C. $\times 55$.

[Whiteley.]

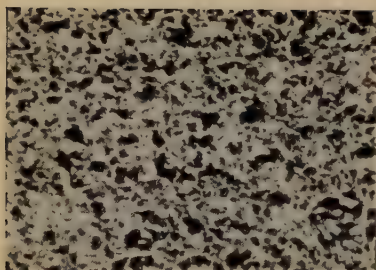


FIG. 34.—Sample No. 3, set A piece, Table VIII., forged, 5 min. at 830° C., furnace-cooled. $\times 55$.

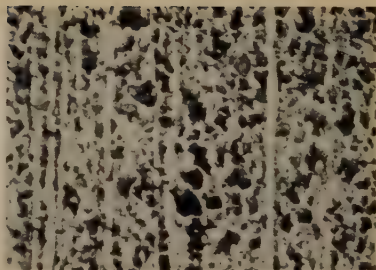


FIG. 35.—Sample No. 3, forged, 5 min. at 830° C., furnace-cooled. $\times 55$.

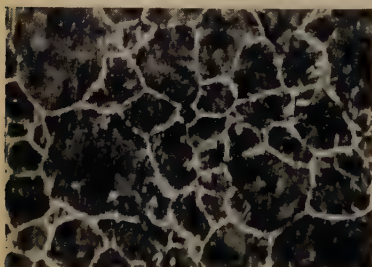


FIG. 36.—Sample No. 1, set A piece, Table VIII., thermally refined, 48 hr. at 930° C. $\times 55$.

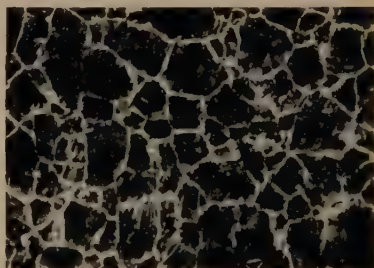


FIG. 37.—Sample No. 1, set A piece, Table VIII., forged, 48 hr. at 930° C. $\times 55$.

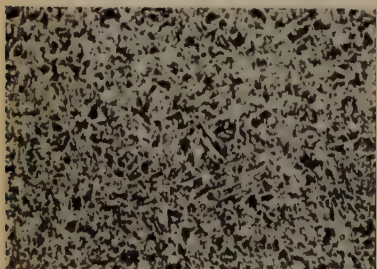


FIG. 38.—Sample No. 6, 5 min. at 830° C. $\times 55$.

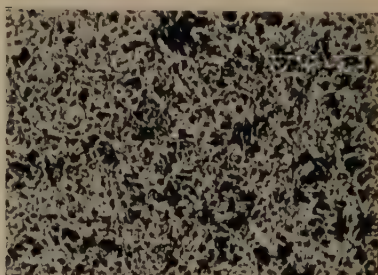


FIG. 39.—Sample No. 6, 18 hr. at 830° C. $\times 55$.

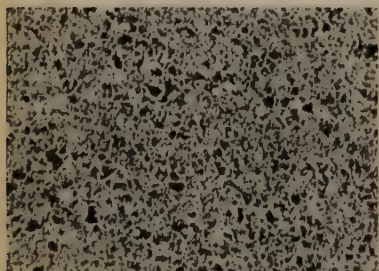


FIG. 40.—Sample No. 6, thermally refined, 168 hr. at 830° C. $\times 55$.

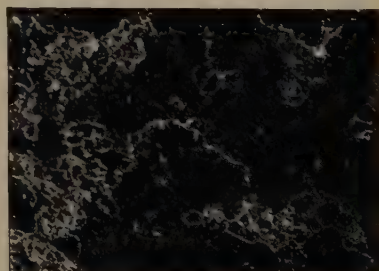


FIG. 41.—Sample No. 6, 27 hr. at 1020° C. $\times 25$.

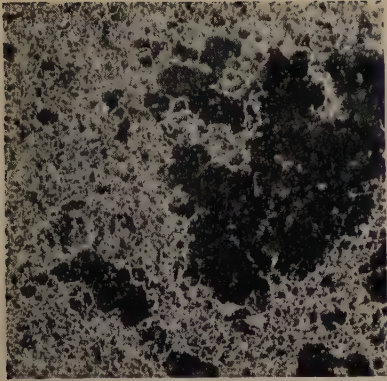


FIG. 42.—Sample No. 6, 11 days at 930° C. $\times 25$.

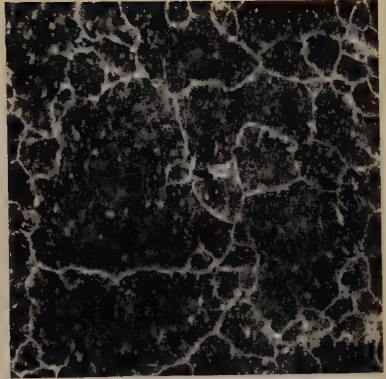


FIG. 43.—Sample No. 6, 6 hr. at 1120° C. $\times 25$.

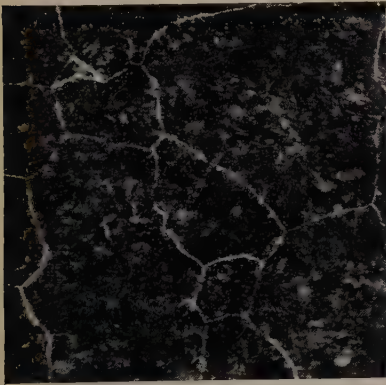


FIG. 44.—Sample No. 6, 6 hr. at 1270° C. $\times 25$.

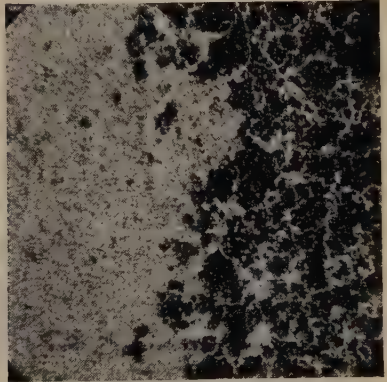


FIG. 45.—Sample No. 5, gradient heating through Ac_1 and 1 hr. at 1000° C. $\times 16$.

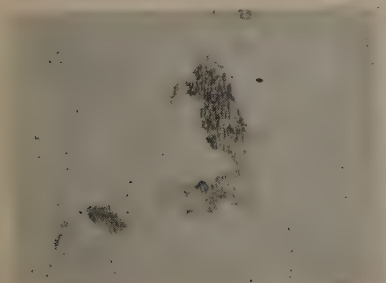


FIG. 46.—Sample No. 5, quenched at Ac_1 during rapid heating. $\times 900$.

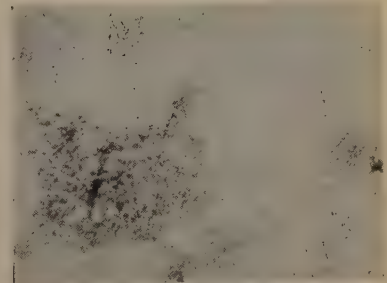


FIG. 47.—Sample No. 5, quenched at Ac_1 during slow heating. $\times 900$.

[Whiteley.]

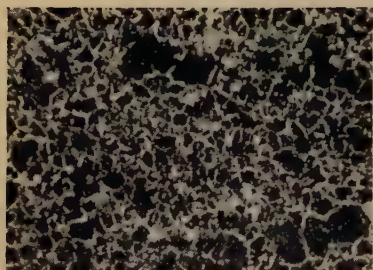


FIG. 48.—Sample No. 1, heated slowly to 790° C. and 2 min. at 930° C. $\times 55$.

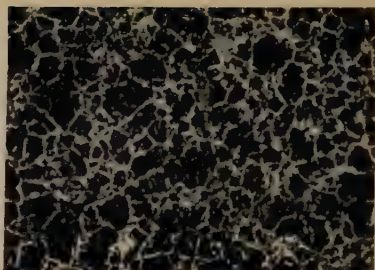


FIG. 49.—Sample No. 1, rapidly heated, 2 min. at 930° C. $\times 55$.

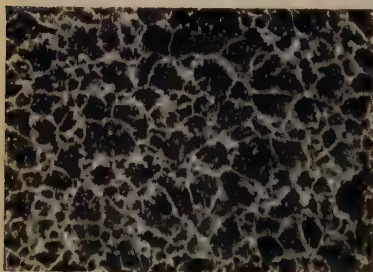


FIG. 50.—Sample No. 6, very rapidly heated, 6 hr. at 1120° C. $\times 25$.

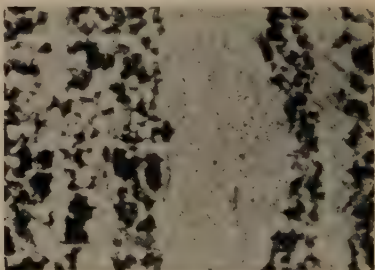


FIG. 51.—Sample No. 6, forged, cooled from 830° to 650° C. in 5 hr. $\times 120$.

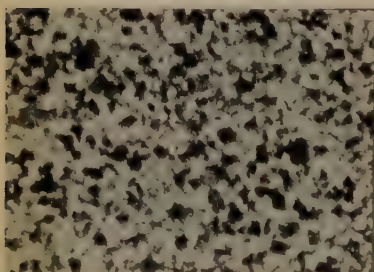


FIG. 52.—Sample No. 6, forged, 2 hr. at 1250° C., cooled from 830° to 650° C. in 5 hr. $\times 120$.

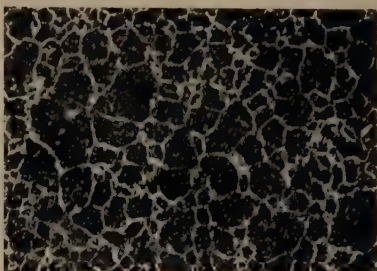


FIG. 53.—Sample No. 6, forged, 6 hr. at 1120° C. $\times 25$.



FIG. 54.—Sample No. 6, forged, very rapidly heated, 6 hr. at 1120° C. $\times 25$.



FIG. 55.—Samples Nos. 3 and 3E, welded, 30 min. at 1350° C., 30 min. at 930° C. $\times 85$.

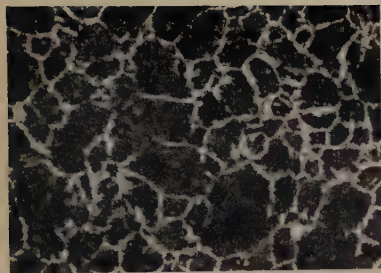


FIG. 56.—Sample No. 3, forged, 45 min. at 960° C. $\times 55$.

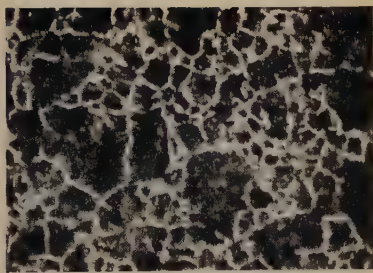


FIG. 57.—Sample No. 3B, forged, 45 min. at 960° C. $\times 55$.

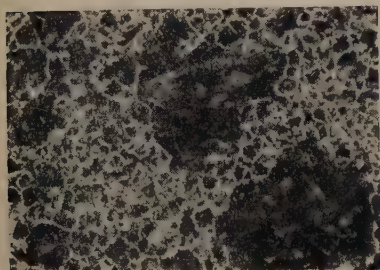


FIG. 58.—Sample No. 3C, forged, 45 min. at 960° C. $\times 55$.

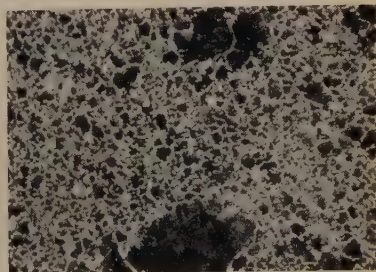


FIG. 59.—Sample No. 3D, forged, 45 min. at 960° C. $\times 55$.

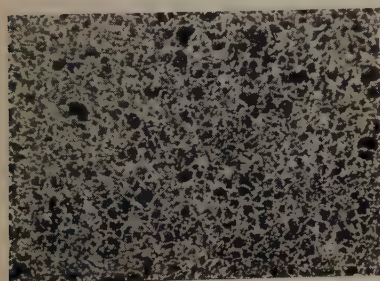


FIG. 60.—Sample No. 3E, forged, 45 min. at 960° C. $\times 55$.

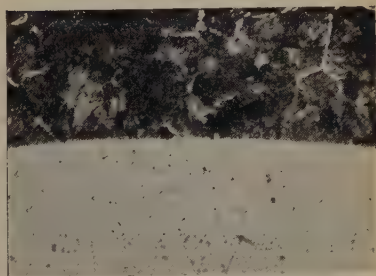


FIG. 61.—Sample No. 1, aluminium core, 2 hr. at 1000° C., 30 min. at 930° C. $\times 85$.

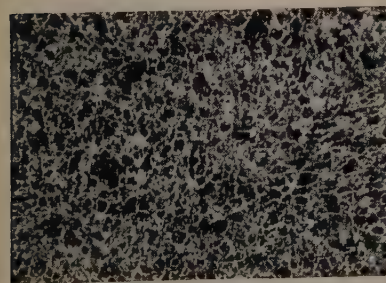


FIG. 62.—Sample No. 1, 15 min. at 1390° C., air-cooled, 30 min. at 930° C. $\times 55$.

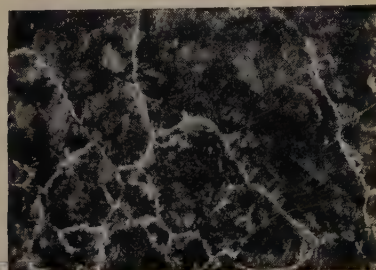


FIG. 63.—Sample No. 1, 15 min. at 1390° C., slowly cooled, 30 min. at 930° C. $\times 55$.

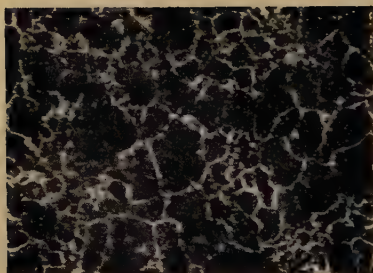


FIG. 64.—Sample No. 3, preheated to 1170° C., 90 min. at 930° C. $\times 25$.

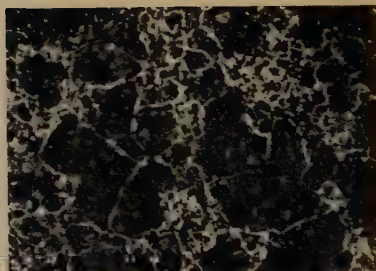


FIG. 65.—Sample No. 3, preheated to 1250° C., 90 min. at 930° C. $\times 25$.

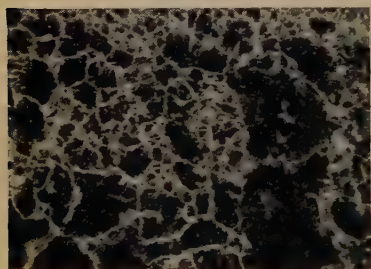


FIG. 66.—Sample No. 3, preheated to 1300° C., 90 min. at 930° C. $\times 25$.

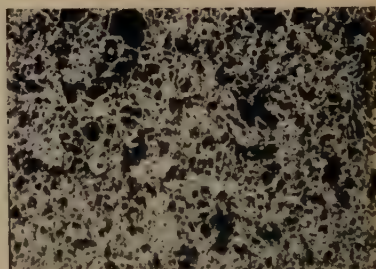


FIG. 67.—Sample No. 3, preheated to 1350° C., 90 min. at 930° C. $\times 25$.

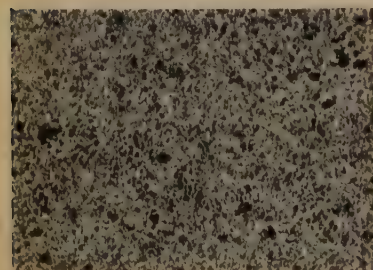


FIG. 68.—Sample No. 3, preheated to 1400° C., 90 min. at 930° C. $\times 25$.



FIG. 69.—Sample No. 1, preheated to 1400° C., 43 hr. at 930° C. $\times 25$.



FIG. 70.—Sample No. 9, pit sample, 72 hr. at 930° C. $\times 55$.

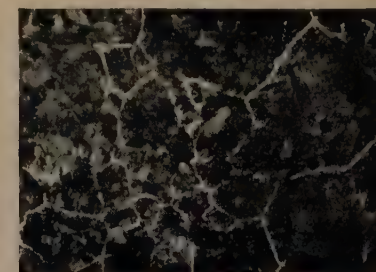


FIG. 71.—Sample No. 9, billet, 5 hr. at 930° C. $\times 55$.

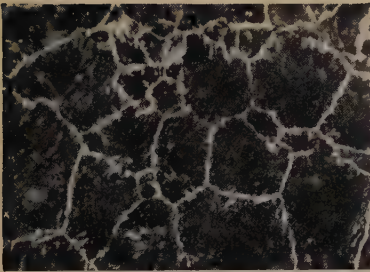


FIG. 72.—Sample No. 3D, spheroidised, 4 hr. at 1120° C. × 55.

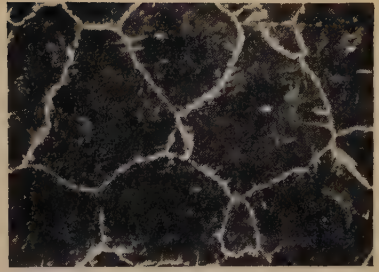


FIG. 73.—Sample No. 3D, as-rolled, 4 hr. at 1120° C. × 55.

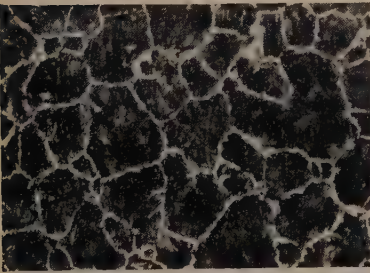


FIG. 74.—Sample No. 8, forged, 2 hr. at 1150° C., withdrawn 720° C., 5 hr. at 1130° C., rapidly heated. × 55.

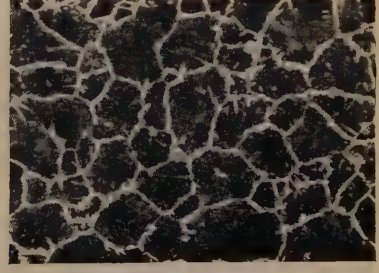


FIG. 75.—Sample No. 8, forged, 2 hr. at 1150° C., furnace-cooled, 5 hr. at 1130° C., rapidly heated. × 55.

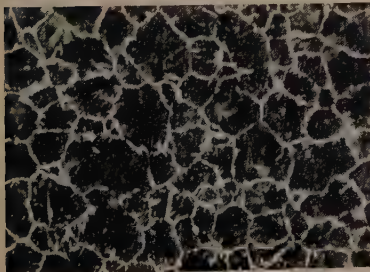


FIG. 76.—Sample No. 8, forged, 2 hr. at 1150° C., cooled from 720° to 650° C. in 2½ hr., 5 hr. at 1130° C., rapidly heated. × 55.

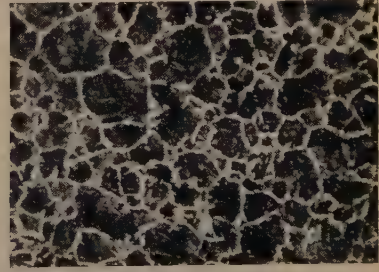


FIG. 77.—Sample No. 8, forged, 2 hr. at 1150° C., furnace-cooled, spheroidised, 5 hr. at 1130° C., rapidly heated. × 55.

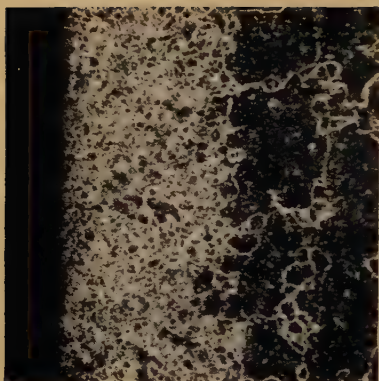


FIG. 78.—Sample No. 6, 72 hr. at 1000° C.
Marginal grains. $\times 25$.

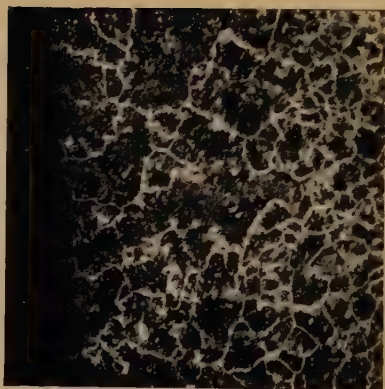


FIG. 79.—Sample No. 6, quenched and tempered,
5 hr. at 1130° C. Marginal grains. $\times 25$.



FIG. 80.—Sample No. 1, aluminium core,
10 min. at 1350° C. $\times 85$.

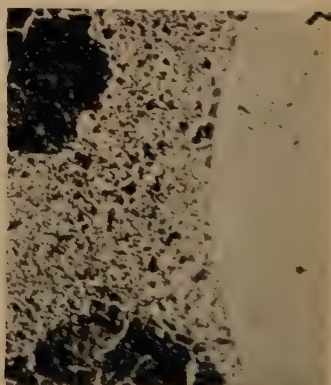


FIG. 81.—Sample No. 1, aluminium core,
45 min. at 1370° C. $\times 85$.

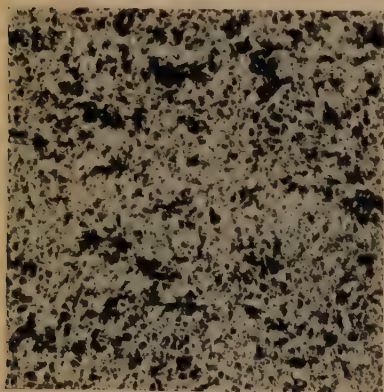


FIG. 82.—Acid Bath Sample, as-cast, 30 min. at
1200° C. $\times 25$.

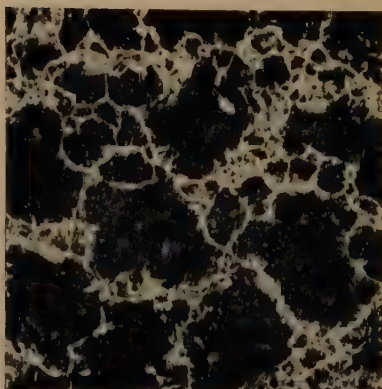


FIG. 83.—Acid Bath Sample, preheated to 1350° C.,
slowly cooled, 30 min. at 1200° C. $\times 25$.

sizes was again observed, as is shown in the last column of Table XXIV.

TABLE XXIV.—*Enlargement of Grain Size with Increasing Aluminium Content.*

Sample No.	Aluminium added per Ton. Oz.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
		As-rolled.	Refined twice and then 4 hr. at 1130° C.
3	Nil	52	...
3A	1	49	53
3B	3	46	45
3C	9	31	35
3D	16	17	28
3E	32	16	...

SECTION 6, *dealing with the Effect of the Rate of Cooling to 1200° C. on Growth in Course-Grained Steels.*

As already remarked, the outstanding feature in steels made fine-grained by the addition of aluminium was the prolonged interruption in their grain growth at the stage immediately following the critical-range refinement; otherwise, development was influenced by factors such as the rate of heating and the initial grain size in much the same way as in the coarse-grained steels. Yet, even the halt itself was not absolutely distinctive, for it was found that, under certain conditions of treatment, a similar state of inactivity could also occur in the samples containing no aluminium. The first hint of this was derived in examining the rates of growth in the Table VIII. set *A* pieces which had been preheated for 4 hr. at about 1300° C. In them, as was stated earlier, unmistakable dominant growth took a considerably longer time to appear than in the as-rolled samples, and, moreover, the mixed grain sizes which then developed strongly resembled those formed in the fine-grained steels after the halt had ended. Later, another and still greater divergence from the normal behaviour of the coarse-grained steels was encountered in a section of sample No. 1 which had been heated to the point of incipient fusion. Although this piece had a very large grain size, it gave a uniformly small one when heated for two days at 930° C. This observation, taken in conjunction with the other, seemed to indicate that the mode of growth in coarse-grained steels was not unalterable, but could be changed by pretreatment at a very high temperature into that which characterised fine-grained steels. At any rate, further enquiry was obviously needed.

To begin with, pairs of sections from samples Nos. 1 and 3 were heated in closed silica tubes for 30 min. at 1170°, 1250°, 1300°

and 1350° C., after which they were cooled at a normalising rate by transference to a furnace standing at 600° C. Also, two roughly 2-lb. blocks were cut from each of the above samples and, after being well coated with a fire cement, were heated for 15 min. at 1350° C. in a Meker furnace, whereupon one pair was withdrawn while the other was further heated to an optically measured temperature of 1400° C., so as to enter the solidus-liquidus range. On removal from the furnace all four blocks were air-cooled. That partial fusion had taken place in the two heated at 1400° C. was shown by subsequent micro-examination, for in both of them the well-known burnt structure was found, whereas no trace of it was discoverable in the 1350° C. blocks or in the two sections which had been heated to that temperature in a closed silica tube.

Having prepared these pieces, the rate of growth in each one was first examined at 930° C. by heating specimens there for progressively longer periods ranging from 10 min. to 43 hr. In the 1170° C. pieces development proceeded in precisely the same way as in the as-rolled samples; no delay in growth was noticeable. In the 1250° C. pieces that was not the case, for in the 10-min. test very little growth was to be seen in either sample and only a few grains had become really dominant in the 30-min. test. Thereafter, the structures tended towards the mixed type, about one-third of the small grains remaining after 90 min., about one-fourth after 4 hr., and none after 15 hr. Growth in the 1300° C. pieces was slower still; in fact it resembled closely that previously observed in the set A pieces of Table VIII., as described in Section 4. In all four 1350° C. pieces a halt had apparently occurred, for their grain sizes in the 90-min. test were nearly as small as in the 10-min. test; a period of more than 24 hr. was needed for full growth, whereas in the 1300° C. pieces 15 hr. sufficed. A halt was unmistakable in the specimens from the 1400° C. pieces, since the grain sizes in all the tests up to and including that of 15 hr. were equally small. Even in the 43-hr. test only the slight dominant growth shown in Fig. 69 had taken place. Thus, starting with the 1170° C. pieces, there was a progressive retardation of growth, and to illustrate it the structures formed in the 90-min. test on sample No. 3 are shown in Figs. 64 to 68, in the order

TABLE XXV.—*Grain Growth at 930° C. in Preheated Coarse-Grained Samples Nos. 1 and 3.*

Preheating Temp. ° C.	Heating Period at 930° C.					
	10 min.	30 min.	90 min.	4 hr.	15 hr.	43 hr.
1170	Started	Growth	More growth	Nearly complete	Complete	...
1250	Started	$\frac{1}{2}$ grown	$\frac{3}{4}$ grown	$\frac{3}{4}$ grown	Complete	...
1300	Small	$\frac{1}{10}$ grown	$\frac{1}{2}$ grown	$\frac{3}{4}$ grown	Complete	...
1350	Small	Small	Slight growth	$\frac{1}{2}$ grown	$\frac{3}{4}$ grown	Complete
1400	Small	Small	Small	Small	Small	Started

of increasing preheating temperature. Also, in Table XXV. the whole of the results are stated concisely by giving visual estimates of the extent to which the dominant grains had developed when mixed grain sizes were produced.

A similar set of tests was then made at 1000° C. Again a gradual diminution in the speed of development was found, the change in the modes of growth in the pieces being very like that disclosed in the 930° C. tests except that the rates of growth were faster. The results are set out in the same brief manner in Table XXVI.

TABLE XXVI.—*Grain Growth at 1000° C. in Preheated Coarse-Grained Samples Nos. 1 and 3.*

Preheating Temp. ° C.	Heating Period at 1000° C.			
	10 min.	1 hr.	4 hr.	16 hr.
1250	$\frac{3}{4}$ grown	Nearly complete	Complete	...
1300	$\frac{3}{4}$ grown	$\frac{5}{8}$ grown	Complete	...
1350	$\frac{1}{10}$ grown	$\frac{1}{10}$ grown	$\frac{3}{4}$ grown	Complete
1400	Small	Small	Small	$\frac{1}{4}$ grown

Two rapid-heating tests were next carried out in which one set of specimens from the four 1350° and 1400° C. blocks was held for 5 hr. at 930° C. and another set for 5 hr. at 1000° C. In all instances the small grain sizes obtained were indistinguishable from those given by similarly treated specimens of the as-rolled fine-grained-steel samples Nos. 6 and 7. Lastly, the rates of growth were compared in doubly refined sections of the 1170°, 1350° and 1400° C. pieces, the specimens being heated at 930° C. for varying periods. Again growth was much more rapid in the 1170° C. pieces than in either the 1350° or the 1400° C. blocks. The difference is shown in Table XXVII. and more precisely in Table XXVIII., where the sample No. 3 grain sizes as determined by the counting method are recorded. On comparing Tables XXV. and XXVII. it will be seen that the small initial grain size had the usual effect of shortening the halt.

These several tests thus demonstrated that as the preheating

TABLE XXVII.—*Grain Growth at 930° C. in Preheated Coarse-Grained Samples after a Double Refinement at 850° C.*

Preheating Temp. ° C.	Heating Period at 930° C.			
	30 min.	90 min.	7 hr.	48 hr.
1170	Growth	More growth	Complete	...
1350	$\frac{1}{4}$ growth	$\frac{1}{4}$ grown	$\frac{3}{4}$ grown	Complete
1400	Small	Small	Growth started	$\frac{1}{4}$ grown

temperature was raised from about 1200° to 1400° C. and the subsequent rate of cooling was fairly rapid, the mode of grain growth in coarse-grained steels was progressively altered, until it resembled that exhibited in steels rendered fine-grained by the addition of

TABLE XXVIII.—*Grain Sizes formed at 930° C. in Preheated Pieces of Sample No. 3 after Double Refinement at 850° C.*

Preheating Temp. ° C.	Heating Period at 930° C.			
	30 min.	90 min.	7 hr.	48 hr.
1170	141	89	56	52
1350	940 *	416 *	82	45
1400	2100	2100	1090 *	200 *

* Mixed grain sizes.

aluminium. But, having reached that conclusion, the enquiry could not be left there, for the coarse-grained steels after casting had passed through the temperature range where the change was induced, so that either the preheating treatment in that region was the cause or else a transition from the fine-grained to the coarse-grained variety of steel took place during the relatively slow cooling of the ingot after solidification. The latter certainly seemed to be the more likely explanation, since cold ingots to be rolled or forged and not containing aluminium were often reheated to 1250° C. or even higher and yet the finished steel was coarse-grained. Before examining the influence of the cooling rate on growth, however, specimens of the 1350° and 1400° C. blocks were heated for 6 hr. at 1170° C., furnace-cooled and again heated for 30 min. at 930° C. The object of this treatment was to ascertain whether the normal mode of grain growth could be restored by holding the preheated samples at a temperature not far below that at which the conversion to the fine-grained condition had been found to start. As is shown

TABLE XXIX.—*Grain Growth in the 1350° and 1400° C. Blocks after Treatment for 6 hr. at 1170° C.*

Sample.	Growth in 30 min. at 930° C.
No. 1, 1350° C. block	Half grown
No. 3, " "	Half grown
No. 1, 1400° C. block	One-tenth grown
No. 3, " "	One-tenth grown

in Table XXIX., only a partial reversal occurred, the rate of growth in the 1400° C. block being now comparable with that indicated for the 1300° C. pieces in Table XXV.

The speed of cooling from the solidus point thus appeared to be

the controlling factor in the change, and, in order to confirm this inference, some further tests were made in the following way: Two sections from each of the samples Nos. 1 and 3 were heated in pairs, in closed silica tubes, for 15 min. at 1390° C., after which one pair (X) was quickly transferred to a furnace standing at 600° C., while the temperature of the other pair (Y) was lowered in 5 min. to 1300° C. and then very gradually during 5 hr. to 1170° C., whereupon that pair was likewise placed in the furnace at 600° C. A third pair of sections (Z) was also heated for 15 min. at 1390° C., but this time the temperature was reduced in 5 min. to 1170° C., where the pieces remained for 2 hr., after which they were cooled in 2 hr. to 900° C. and finally in the same manner as the X and Y pairs.

Having prepared these sections so that only the rates at which they had been cooled varied, specimens from all six were heated for 30 min. at 930° C. in order to compare their modes of grain growth. As was expected, the grain sizes which formed in the quickly cooled X specimens were no larger than those given by the 1350° and 1400° C. blocks when similarly treated. That produced in sample No. 1 is illustrated in Fig. 62. Subsequently, the halt in the X sections was found to last about 12 hr. at 930° C., a period roughly midway between the lengths of the halts in the 1350° and in the 1400° C. blocks. The Y specimens were strikingly different, for in both cases development had progressed to the extent shown in Fig. 63. No indication of the halt which had occurred in the X sections was to be seen, and its total elimination by the slow cooling to 1170° C. was placed beyond doubt when specimens were heated for only 10 min. at 930° C., for, even then, their grain sizes were quite large. In the Z specimens mixed grain sizes appeared closely resembling those obtained in the same test on sections of the 1400° C. blocks which had been reheated for 6 hr. at 1170° C., as recorded in Table XXIX. Hence, in the Z sections the coarse-grained condition had been but partially restored. As a further illustration of these changes, the grain sizes of all six specimens, after 30 min. at 930° C., are given in Table XXX.

TABLE XXX.—*Grain Sizes Produced in 30 min. at 930° C. in Samples Nos. 1 and 3 after being Heated at 1390° C. and Cooled at Different Rates.*

Section.	Treatment.	Rate of Cooling.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
			Sample No. 1.	Sample No. 3.
X	15 min. at 1390° C.	Normalising	1500	1600
Y		Very slowly to 1170° C.	19	28
Z		Quickly to 1170° C. and very slowly to 900° C.	140	165

Thus the conclusion emerged that the mode of grain growth in highly preheated coarse-grained steels was determined by the rate at which they were cooled to 1200°C . For development on reheating to proceed in the normal way the temperature should not fall to the above point too rapidly. The limiting rate was not ascertained, however; all that can be said is that the type of growth characteristic of fine-grained steels was increasingly exhibited as the preheating temperature was raised above 1200°C ., provided that the subsequent cooling to below 1200°C . took place in a few minutes.

The next and final step in the enquiry was to examine the mode of growth in coarse-grained steels which had been quickly cooled from the liquid state. For this purpose, ordinary ladle samples were used. Two were obtained, one from an acid and the other from a basic cast, these being samples Nos. 9 and 10 in Table I. By knocking them out of the pot at about 1350°C . their temperature dropped within 1 min. to below 1100°C . Samples representative of slow cooling from the molten condition were taken from the $3\frac{1}{2}$ -in. billets into which the 3-ton ingots of both the casts had been rolled. First of all, specimens from the four samples were heated for 30 min. at 930°C ., since this particular test had been found very suitable for indicating the mode of grain development. The result was as anticipated. In the billet specimens growth was well advanced and corresponded closely with that observed in the same test on the as-rolled coarse-grained samples Nos. 1, 2 and 3. In the ladle-sample specimens a much smaller grain size was present, notwithstanding that their initial grain sizes were extremely large. Apparently, a halt in growth had occurred, an inference which was fully confirmed when a second test of 5 hr. at 930°C . was made, for no perceptible increase in the grain sizes took place. Further tests on the ladle samples then showed that the halt at 930°C . continued for at least three days. The grain size of sample No. 9 after this last treatment is illustrated in Fig. 70; that produced in the billet sample when heated for 5 hr. at 930°C . is shown in Fig. 71.

At 1000°C . the halt in the ladle samples lasted about 5 hr.; thereafter, at that temperature growth proceeded slowly and was still incomplete when a state of virtual stability was reached. Even after 3 hr. at 1100°C . the dominant grains were not fully developed, and to eliminate all the residual small grains a temperature approaching 1200°C . was needed. The wide disparity between the grain sizes given by the billet and ladle samples in these tests can be seen in Table XXXI. Growth in the ladle samples was, in fact, indistinguishable from that in the 1400°C . blocks, whereas in the billet samples it was perfectly normal for coarse-grained steels. A similar difference was obtained when the effects of rapid heating and of a small initial grain size were examined. One example of the grain sizes produced at 970°C . in doubly refined specimens is included in Table XXXI.

It was thus clear that the rate at which coarse-grained steels

cooled from either the liquid or the solid condition to 1200° C. determined the mode of their grain development when the austenitic range was re-entered. Apparently, the presence of aluminium in sufficient amount prevents or else greatly retards the transition to the coarse-grained class, even when the steel is very slowly cooled and as a consequence it remains fine-grained in character. The explanation of the high-temperature change which occurs in the

TABLE XXXI.—*Differences between Grain Sizes Produced in Slowly and Quickly Cooled Samples of the Same Casts.*

Treatment.	Average Number of Grains in 10 sq. in. at 100 Magnification.			
	Sample No. 9.		Sample No. 10.	
	Ladle.	Billet.	Ladle.	Billet.
Initial grain size	3	41	4.5	96
2 hr. at 1000° C. . . .	720	27	480	39
16 „ 1000° C. . . .	224 *	22	220 *	26
3 „ 1100° C. . . .	192 *	18	202 *	21
2 „ 1200° C. . . .	17	...	14	...
Refined and 90 min. at 970° C.	800	45

* Mixed grain sizes.

absence of aluminium is by no means obvious, but the tentative suggestion is offered that slow cooling allows time for a manganese reaction of some sort to take place whereby the steel becomes coarse-grained. For one thing, any FeS remaining at the end of solidification is converted to MnS, provided that the manganese content is adequate, but whether this particular reaction affects the mode of grain growth exhibited by the steel cannot at present be stated.

That a normal manganese content does assist the production of a coarse-grained steel seemed to be indicated when growth was examined in two bath samples containing only 0.05% of that element. They were taken from acid casts just before the final silicon addition, when the carbon had dropped to 0.45% and the amount of iron in the slag was about 13.0%. In dealing with these samples, the treatment which had been found to bring about the reversal in aluminium-free steels was first given. A section from each was heated for 15 min. at 1350° C., the temperature being then gradually lowered in 1½ hr. from 1300° to 1150° C., whereupon one section was cooled in air and the other in the furnace. This procedure now entirely failed to induce a coarse-grained mode of growth, for specimens from both sections had a very small grain size even after they had been heated for 24 hr. at 1000° C. In fact, so extended was the halt that at 1120° C. a period of at least 3 hr. was needed to start dominant growth. Moreover, after a double refinement at 930° C. the halt was

still lengthy at $1000^{\circ}\text{C}.$, so that there could be no question that the bath samples were fine-grained in character. Yet similarly preheated and slowly cooled sections of the pit samples, which contained about 0.80% of manganese, were thoroughly coarse-grained. There was thus good reason to infer that this difference was due to the manganese addition. Apparently even the small amount of manganese in the bath samples was not without some action, for in a test of 30 min. duration at $1200^{\circ}\text{C}.$ dominant growth had barely begun in specimens of the samples as cast, whereas in those from the preheated sections it was well on the way to completion. The two structures are illustrated respectively in Figs. 82 and 83.

SECTION 7, *dealing with the Influence of the Carbide Condition on Growth.*

Of the several factors which were found to affect austenitic grain growth, but one now remains to be considered, *viz.*; the state of the carbide in the steel as the critical range is entered. Although this variable could not be entirely dissociated from that of the heating rate, it had hitherto been kept as constant as possible by confining the tests to samples containing a clearly defined lamellar pearlite. But cementite may also exist in steel as small globular particles, and when they preponderate grain development can take quite a different course. The rates of growth, the grain sizes attained, the effects of initial grain size as well as the lengths of the halt in fine-grained steels may be greatly altered, the complexities involved being indeed so numerous that only a very limited investigation of this factor could be attempted. There are two well-known ways of producing spheroidal cementite; steel when in the pearlitic condition may either be heated for a long while at a temperature just beneath the lower critical point, or it may be quenched from the austenitic range and then tempered at about $700^{\circ}\text{C}.$ In the tests to be described both methods were employed, the former being denoted whenever the term spheroidisation is used.

It was particularly essential for a proper comparison of growth when examining the influence of the state of the carbide that in each set of tests the specimens of any one sample should have the same initial grain size. In preparing them, therefore, all were heated together, and, having produced a large or small grain size as required, some were water-quenched and the rest cooled at various slower rates through the critical range. Quenched specimens to be tempered were then held for two days at $700^{\circ}\text{C}.$, while pearlitic specimens to be spheroidised were given a three-day treatment at that temperature. For the latter process furnace-cooled pieces were always taken. In the tempered specimens the carbide was invariably found to be globularised to the extent that the particles were easily visible at a magnification of 150 diameters. Particles of a similar magnitude were likewise formed in the spheroidised

specimens, but their distribution was, of course, not so uniform, owing to the presence of pro-eutectoid ferrite. It was noticed repeatedly that spheroidisation took place more readily when the grain sizes were small, for in such cases the divorce was complete, whereas in specimens with large grain sizes traces of lamellar pearlite remained.

To illustrate the effect of the state of the cementite on growth in coarse-grained steels, it will be sufficient to give the results of some tests which were made at 930° and 1000° C. on specimens of samples Nos. 1 and 10 in the furnace-cooled, spheroidised and quenched conditions, with three widely separated initial grain sizes. The largest were produced by heating the specimens for 2 hr. at 1150° C. and the smallest by a double refinement at 850° C., while the as-rolled samples provided the intermediate sizes. In order to ensure the attainment of virtual stability in the tests, the heating was continued for 48 hr. at 930° C. and for 24 hr. at 1000° C. The

TABLE XXXII.—*Effects of Spheroidisation and Quenching on Grain Growth at 930° and 1000° C. in the Coarse-Grained Sample No. 1.*

Treatment.	Initial Grain Size.	Average Number of Grains in 10 sq. in. at 100 Magnification.	
		930° C.	1000° C.
2 hr. at 1150° C., furnace-cooled	23	17	15
2 hr. at 1150° C., furnace-cooled, spheroidised	23	30	25
2 hr. at 1150° C., quenched	23	32	29
As-rolled billet *	150	37	28
As-rolled billet, spheroidised	150	44	31
Twice to 850° C., furnace-cooled	640	44	38
Twice to 850° C., furnace-cooled, spheroidised	640	44	37
Twice to 850° C., quenched	640	37	37

* This billet was of smaller section than that used in the previous tests on sample No. 1.

results, together with the initial grain sizes, are shown in Tables XXXII. and XXXIII.

Two things are to be noted in these examples; one is that little variation occurred between the extents of growth in the spheroidised and the quenched specimens, and the other is that in both conditions the influence of the initial grain size was modified considerably. The same features were seen in similarly prepared specimens which had been heated for only 1 hr. at 930° C. Actually, the difference between the sizes of the carbide particles after spheroidising and after quenching when the specimens are submitted to grain-growth tests is not so great as might at first sight appear, for

cementite is precipitated in quenched specimens before the critical range is entered and, during slow heating especially, the dimensions of the particles will increase appreciably.

TABLE XXXIII.—*Effects of Spheroidisation and Quenching on Grain Growth at 930° and 1000° C. in the Coarse-Grained Sample No. 10.*

Treatment.	Initial Grain Size.	Average Number of Grains in 10 sq. in. at 100 Magnification.		
		930° C.	1000° C.	
			Slow Heating.	Rapid Heating.
2 hr. at 1150° C., furnace-cooled .	21	18	15	35
2 hr. at 1150° C., furnace-cooled, spheroidised .	21	44	35	55
2 hr. at 1150° C., quenched .	21	51	32	53
As-rolled billet .	96	30	25	42
As-rolled billet, spheroidised .	96	58	49	55
Twice to 850° C., furnace-cooled .	750	58	45	...
Twice to 850° C., furnace-cooled, spheroidised .	750	64	47	...
Twice to 850° C., quenched .	750	59	44	...

The importance of the state of the carbide as a factor in grain development was still more in evidence when its effect was examined in the fine-grained steels. To begin with, tests were made on the as-rolled samples Nos. 3, 3B, 3C and 3D, since this series included transition stages between coarse- and fine-grained steels. Specimens were spheroidised in the usual way at 700° C. and were then heated together with unspheroidised duplicates for 4 hr. at 1120° C., so as to avoid the formation of mixed grain sizes in Nos. 3C and 3D. The results are stated in Table XXXIV.; they show that in each instance the grain size produced in the spheroidised piece was much

TABLE XXXIV.—*Effect of Spheroidisation on Growth at 1120° C. in No. 3 Samples.*

Sample.	Aluminium Addition. Oz. per ton.	Initial Grain Size.	Average Number of Grains in 10 sq. in. at 100 Magnification.		
			As-Rolled.	Spheroidised.	Ratio.
3	Nil	52	22	48	0.46
3B	3	46	22	50	0.44
3C	9	31	19	44	0.43
3D	16	17	11	32	0.41

the smaller. Moreover, with an increasing aluminium content the disparity widened progressively, as can be seen from the ratios in the last column. The structures formed in the spheroidised and pearlitic specimens of sample No. 3D are illustrated respectively in Figs. 72 and 73.

In the thoroughly fine-grained steels even the degree of fineness of the lamellar pearlite was apparently not without some influence on growth. For example, two pieces of equal dimensions from sample No. 6 were heated for 10 min. at 1200° C., after which one was cooled in air and the other more slowly in the furnace in order to develop a coarser pearlite. A number of tests was then made in

TABLE XXXV.—*Effect of Carbide Condition on Growth at 1130° C. in Refined Fine-Grained Steels.*

Rate of Cooling.	Average Number of Grains in 10 sq. in. at 100 Magnification.			
	Sample No. 6.		Sample No. 7.	
	Rapid Heating.	Slow Heating.	Rapid Heating.	Slow Heating.
Initial grain size	2000	2000	1800	1800
Air-cooled from 930° C.	75	38	71	39
Air-cooled from 710° C.	78	39	71	39
Furnace-cooled, average rate 8° C. per min.	99	40	80	42
Furnace-cooled in 2 hr. from 710° to 650° C.	140	41	99	44
Furnace-cooled, spheroidised	198	98	179	88
Quenched from 930° C.	190	120 *	174	110 *
Quenched from 930° C., tempered	183	125	170	100

* Mixed grain sizes.

which specimens from the two pieces were heated at 1000° C. for periods ranging from 1 hr. to 16 hr., and it was found that, although the mixed grain sizes ultimately attained were not dissimilar, the halt in the air-cooled piece was only 2 hr. in length, being about one-half that in the other.

The susceptibility of growth in fine-grained steels to changes in the state of the carbide was further seen when tests were carried out on specimens which had been cooled from the austenitic region at widely differing rates. The specimens of any one sample were preheated together and were then cooled in pairs at the rates indicated in Tables XXXV. and XXXVI. In these preliminary treatments both small and large grain sizes were developed, the former by a double refinement at 930° C. and the latter by heating for 2 hr. at 1150° C. Specimens withdrawn at once and at 720° C. contained a finely lamellar pearlite; it was definitely coarser in the furnace-

cooled specimens and was partly spheroidised when the temperature had been lowered from 710° to 650° C. at the rate of 0.5° C. per min., especially when the grain sizes were small. A thorough granulation of the carbide in furnace-cooled and quenched specimens was obtained in the manner previously mentioned. After the condition of the carbide in the variously cooled specimens of a series had been examined, one set was heated slowly to 900° C. and then more quickly to 1130° C. When this temperature was reached the duplicate set was rapidly heated by inserting it alongside in the furnace, and after remaining for 5 hr. at 1130° C., so as to eliminate mixed grain sizes, both sets were withdrawn. No less than ten series of tests were made in this way and the results were in satisfactory

TABLE XXXVI.—*Effect of Carbide Condition on Growth at 1130° C. in Fine-Grained Steels with Large Initial Grain Sizes.*

Rate of Cooling.	Average Number of Grains in 10 sq. in. at 100 Magnification.			
	Sample No. 6.		Sample No. 7.	
	Rapid Heating.	Slow Heating.	Rapid Heating.	Slow Heating.
Initial grain size *	49	49	33	33
Air-cooled from 1150° C.	63	19	60	27
Air-cooled from 710° C.	65	18	59	29
Furnace-cooled, average rate 8° C. per min.	75	20	65	29
Furnace-cooled in 2 hr. from 710° to 650° C.	116	20	82	28
Furnace cooled, spheroidised	142	96	149	73
Quenched from 1150° C.	70	62	70	64
Quenched from 1150° C., tempered	29	47	33	48

* The forged condition was used.

agreement. Four examples are given in Tables XXXV. and XXXVI.; the following features were disclosed :

(1) In each series of tests the grain sizes produced in the specimens which had been air-cooled from above 900° and from 720° C. were practically identical. It was concluded, therefore, that growth in medium-carbon steels was not appreciably affected by changes in the amounts of pro-eutectoid ferrite, provided that they were not accompanied by any noticeable alteration in the character of the pearlite.

(2) In the rapidly heated specimens an increasing degree of spheroidisation resulted in a progressive reduction of the grain sizes. That was particularly apparent when the initial grain sizes were small, probably because of the greater amount of spheroidisation which had occurred as the cooling rate was retarded in the preliminary treatment. Typical examples showing this gradual

diminution are given in Figs. 74, 75, 76 and 77; they were taken from sample No. 8 with an initial grain size of 41 and illustrate respectively the structures formed at 1130° C. in the air-cooled, the furnace-cooled, the very slowly cooled to 650° C. and the spheroidised specimens. After a slow heating, complete spheroidisation was needed before a marked lessening of the grain sizes took place. Hence, the widest differences due to the rate of heating were to be seen in the specimens which had been cooled in 2 hr. from 710° to 650° C.

(3) When the initial grain sizes were large the grain sizes in rapidly heated quenched specimens were much smaller than those in the corresponding tempered specimens, and since, when the critical range was entered, the cementite precipitated in the former below Ac_1 would, in all probability, be in a finer state than that in the latter, it seems a reasonable assumption that carbide particle size had some influence on growth. The same inference could also be drawn when the initial grain sizes were small, for in the slowly heated quenched specimens the grain sizes were far from uniform, which was not so in the tempered specimens. Yet, particle size cannot be the only factor involved, since, as shown in the Table XXXVI. series, the grain sizes in the tempered pieces were much larger than those in the spheroidised, notwithstanding that the dimensions of the carbide particles in the two conditions were very similar.

(4) Another peculiar feature was that in slowly heated tempered specimens with an initially large grain size the average dimensions of the grains were definitely smaller than in the rapidly heated specimens. In this respect quenched pieces were less consistent; in some series of tests the grain size of the rapidly heated one was slightly the larger, while in others it was somewhat the smaller, as in the examples given in Table XXXVI. That rapid heating should cause the larger grain size to form in any instance was quite unexpected, for in unquenched samples the reverse had invariably been the case at all temperatures below the point where abnormal growth became prevalent. Clearly, so contradictory a result could not be left unexplained, and some further tests were therefore made on initially large-grained tempered specimens in order to examine the mode of their grain growth at temperatures below 1130° C. It was found to be as follows: After a slow heating through the critical range, the usual halt characteristic of fine-grained steels took place, but, although the initial grain sizes were large, this period of inactivity was much shorter than in the corresponding pearlitic specimens. A mixed grain size began to develop within 30 min. at 930° C., whereas a period of at least six days was needed for dominant growth to start in the furnace-cooled specimens. Also, unlike the mode of growth in the latter, the dominant grains did not steadily extend to a large size such as that illustrated, for example, in Fig. 41; they remained comparatively small, and when growth was completed at about 1000° C.

a regular grain size similar to that shown in Fig. 53 was obtained. Even at 1050° C. this size persisted unaltered for at least 48 hr., so that it was quite evident that a second halt in growth had intervened.

Between 1100° and 1150° C. development began again, the peripheral grains being the first to enlarge, while always after the earlier halt they were the last to grow. This greater activity of the border grains explained the fact that most of the slowly heated initially large-grained tempered specimens in the 1130° C. sets of tests had a smaller grain size within than at the margins. An example is given in Fig. 79. When the tempered specimens were rapidly heated, however, no indication of this second halt could be found at any temperature, even after a rate of only 60° C. per min. Again, the first halt was relatively short, but in the subsequent dominant growth the grains continued to develop until the average size became much larger than that of those present during the second halt in the slowly heated specimens. The explanation of the smaller grain sizes shown by the slowly heated tempered specimens in the 1130° C. tests was thus apparent; they were due to the occurrence of a second halt.

SECTION 8, *describing Attempts to Produce a Fine-Grained Steel by the Diffusion of Aluminium in the Solid Metal.*

In making a fine-grained steel aluminium is, of course, added to the liquid metal, and it therefore seemed worth while to enquire whether a coarse-grained steel could be converted into one that was fine-grained by the introduction of aluminium at a temperature below the solidus point. For the first experiment in this direction samples Nos. 3 and 3E were used, since the only difference between them was that one contained no aluminium and to the other 2 lb. per ton had been added. The following procedure was adopted: A $\frac{1}{4}$ -in. hole was drilled nearly to the base of a $1\frac{1}{4}$ in. \times 1-in. block of the aluminium-free sample and in it was placed a closely fitting cylinder, $\frac{7}{8}$ in. long, of the other sample. A short steel plug was then inserted, and, having made the joint gas-tight with a thick covering of arc-deposited metal, the block was heated to 1050° C., whereupon it was forged down to a $\frac{1}{4}$ -in. flat with the cylinder lying horizontally. On examining a section, the weld thus obtained was found to be quite satisfactory. Except for two extremely thin ferrite lines which traversed the pearlite grains at the weld junctions, there was no indication that the piece was composite. That was, however, strikingly apparent after the section had been heated for 30 min. at 930° C., for a completely fine-grained core was then plainly visible, and under the microscope the structure of the case on either side was seen to be of the normal coarse-grained type, the weld junction being as sharply defined as that shown in Fig. 55.

Now, it had already been observed that the addition of only 3 oz. per ton of aluminium to this steel was sufficient to cause an appreciable delay in growth at 930° C. If, therefore, a similar effect

could be produced in the block part of the welded piece by heating a section at a temperature below 1400°C. , direct evidence would be forthcoming that aluminium had diffused in solid steel and had affected growth in the same way as when added to the liquid steel. The first attempt to bring this about was made at 950°C. , where the section was heated for 48 hr. and furnace-cooled, after which it was heated for 30 min. at 930°C. in order to ascertain whether the mode of growth had been altered in the steel adjacent to the core. As no change was to be seen a second heating was given in which the section was held for 32 hr. at 1100°C. , and again there was no difference after the subsequent 930°C. test. That was also the case after the next heating, which was for 6 hr. at 1250°C. Finally, the section was heated for 30 min. at 1370°C. and then very gradually cooled to 1200°C. so as to ensure that a reversal to the normal mode of growth occurred in the coarse-grained parts. Yet, even then, the width of the fine-grained core had not increased in the slightest degree after the 930°C. test, as was proved by micrometer measurement, nor was there any indication in the contiguous metal of a retardation in grain growth. The two structures with the sharp line of division still present between them after these several heatings are shown in Fig. 55.

Since the above result was completely negative, another experiment was made in the following way: A $\frac{1}{16}$ -in. dia. hole was drilled in a small block of sample No. 1 and in it a closely fitting piece of electrolytically prepared aluminium was inserted. The hole was hermetically sealed by arc welding and the block then heated for 2 hr. at 1000°C. On examining a transverse section after this treatment, the cavity was found to be lined with a layer of a hard material consisting apparently of an iron-aluminium compound, but no perceptible alteration in growth could be seen in the adjacent steel after the usual 30-min. test at 930°C. ; as shown in Fig. 61, it was still entirely coarse-grained. That having been ascertained, the section was heated for 6 hr. at 1250°C. and slowly cooled, but again there was no change. A third heating was therefore given at 1350°C. , where the section was held for 10 min., after which it was very slowly cooled to 1150°C. and then furnace-cooled. At last, when the 930°C. test was applied, a narrow but definite border of fine grains was observed next to the aluminium lining, as illustrated in Fig. 80. With the object of extending this zone, the section was once more heated, this time for 45 min. at 1370°C. , after which it was cooled as in the previous instance and then reheated for 3 hr. at 930°C. in order to make quite certain that the fine-grained condition had actually been produced. That was now unmistakably clear, for the zone of small grains had spread outwards to a considerable distance but not uniformly; three or four arms protruded into the surrounding coarse-grained steel, one of which is partly shown in Fig. 81. This mode of advance suggested that liquefaction had occurred, although no indication of fusion was noticeable either

in the cavity or structurally. Nevertheless, it was undoubtedly open to question as to whether the fine-grained areas had been formed solely by the diffusion of aluminium into the solid steel, and the result was consequently inconclusive.

The author wishes to express his indebtedness to Mr. G. Wortley for considerable help afforded during the investigation.

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DISCUSSION.

Dr. C. H. DESCH, F.R.S. (Vice-President, London): This interesting paper contains a mass of very valuable information. The author has the same capacity which distinguished Dr. Stead for getting valuable results out of a few small specimens. In this case the number of specimens is large, but from these little specimens of 0.8 g. he gets more information than most of us could obtain from quite large masses.

I find the paper a difficult one to study, because, whilst every sentence and statement in it is perfectly clear, there is some difficulty in seeing the wood for the trees, and it is not easy to draw general conclusions. One fact which comes out clearly, that by this high-temperature heating an inherently coarse-grained steel can be converted into one having similar properties to an aluminium-treated steel, is of considerable importance. In the last part of the paper, the author shows that the effect of aluminium is not due to aluminium in solid solution; I think that one must accept

that, although he does not wish to be dogmatic on the subject. On the other hand, he does not think that the ordinary particles of aluminium oxide will account for the effect.

There is, it seems to me, a possibility that very fine intercrystalline films may play a considerable part, and these are of such a character that they are not to be seen by microscopical examination under ordinary powers. I think that there is still a great deal to be done in the detailed study of steels of this kind under very high magnifications, with, of course, very special precautions in preparing the surfaces.

The facts contained in the paper, and the curves which are given, representing the grain growth with temperature, are extremely interesting. The fact that the refining takes place essentially at the Ac_1 point is brought out clearly, and I think that that must have considerable practical consequences.

The mass of detail is, as I say, so great that it is difficult to express a general opinion, and so I shall only express my own appreciation of the great value of this very extensive research, which has involved the examination of an enormous number of specimens and the carrying out of a large number of heat treatments under carefully controlled conditions.

Dr. T. SWINDEN (Member of Council; Central Research Department, The United Steel Companies, Ltd., Stocksbridge, near Sheffield): I welcome this paper very heartily. The author has mentioned a paper which Mr. Bolsover and I presented to the Institute in Düsseldorf in 1936, and I think that it is fair comment to say that the results given in that paper were received with a good deal of scepticism, even on the part of the present author. We had been working on this subject at Stocksbridge for some three years before the publication of that paper, and at that time these controlled-grain-size steels were in considerable commercial production. We said very frankly on that occasion that a great deal more work required to be done to explain the results. I did not know that Mr. Whiteley had been working so intensively on this subject from that time onwards, but if one were to choose someone to do the work one could not choose anyone better than Mr. Whiteley, who is able to deal with a subject of this kind with meticulous care and thoroughness. I regard this paper as a classic on this subject.

One point which was criticised in 1936 was the use of the McQuaid-Ehn test for inherent grain size. This, as you know, consists of heating the steel in a carburising medium at 927°C . (1700°F). It was pointed out that this was neither a forging temperature nor a treating temperature; why therefore, it was asked, should it be used? I think that the work of the present author does amply justify the selection of a temperature about that region for a general test, but he has indicated that there are other factors which should be taken into consideration in getting at the whole truth even about

inherent grain size. The work appears to be in full support of his hypothesis that the carbide size is at least a very important and controlling factor, but the question still remains of how the addition of aluminium affects that.

There are three theories : One is the effect of aluminium in solution, another the nucleation theory, and the third the possible effect on grain boundaries ; and the latter, it may be remembered, was enlarged upon at some length by Dr. Benedicks in discussing our paper in 1936. I do not propose to discuss which is the correct hypothesis, but I hope that Mr. Whiteley will be prevailed upon to continue this work, with a view to explaining further the obvious effect of aluminium in controlling the growth of grains on reheating beyond the Ac_1 point.

Dr. A. McCANCE (Vice-President ; Messrs. Colvilles, Ltd., Glasgow) : I am not as yet in a position to criticise this paper, since it requires a great deal more study than I have been able to give it, but I should like to join with previous speakers in paying tribute to the author for his excellent work.

(Contributed later in writing.) It is possible to put the study of crystal growth on a more quantitative basis and to explain the mass of information now known in the light of principles already accepted. For this purpose, the new information gathered so systematically by Mr. Whiteley will prove helpful.

If a metal contains N crystals per unit volume, the probability of one crystal uniting with a second will be proportional to $(N - 1)$, since this will be a measure of the number in any small volume which surrounds and includes the crystal in question. The rate of growth measured by the diminution in crystal number will depend on this probability, so it can be stated :

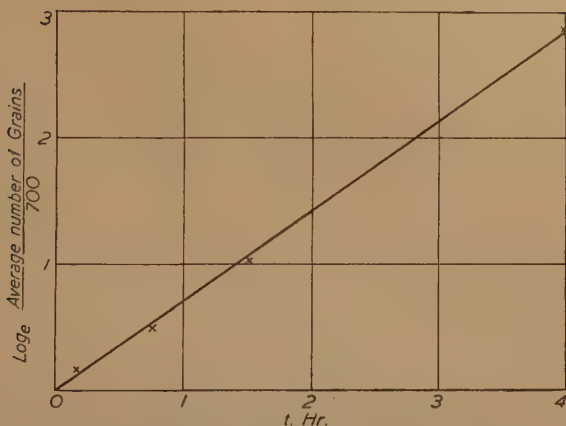
$$-\frac{dN}{dt} = K(N - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K is the velocity of growth defined as the number of unit crystals which coalesce each second. When the whole volume is made up of a single crystal, this expression gives correctly the zero rate of increase which is self-evident in such a case. On integrating, the number of crystals N after time t , starting with an initial number N_0 , is given by :

$$\log \frac{N - 1}{N_0 - 1} = -Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

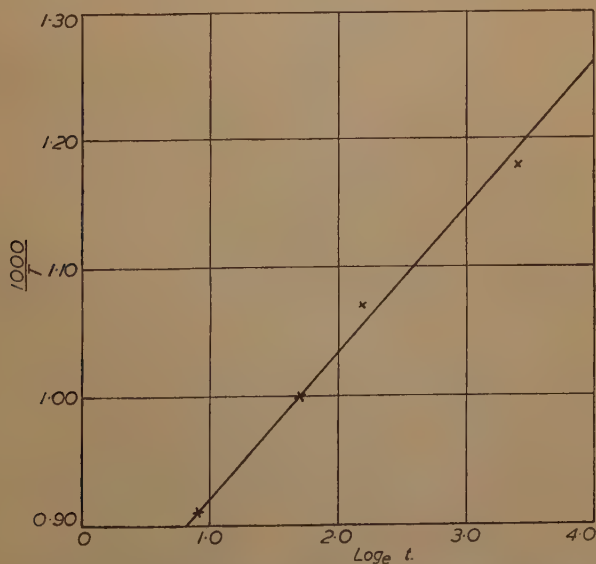
The results given in Fig. 5 have been plotted in this way in Fig. A, taking $(N_0 - 1)$ as about 700, and the points do lie on a reasonably straight line.

From the shape of some of Mr. Whiteley's curves it appears as if certain of the steels that he used would never grow into a single crystal aggregate, but that the growth would stop when the number

FIG. A.—Variation of Number of Grains with Time t .

of crystals per unit volume was still substantial. This behaviour is well illustrated in Fig. 6, and it immediately raises questions regarding the effect of forging, composition, deoxidation practice, &c., on the residual crystal density as well as on the rate of growth.

Several examples have been given in the paper of the effect of

FIG. B.—Variation of Time of Growth t with Temperature T .

temperature on the rate of growth, and it has been demonstrated that the time taken for apparent growth to stop lengthens appreciably as the temperature falls. Assuming that growth ceases to be observable after a given percentage of crystals have coalesced, equation (2) would then state that $Kt = \text{constant}$. Now, it has been found that reaction velocities, similar in type to that of crystal growth above, can generally be represented by an equation of the form :

$$\log K = \frac{A}{T} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and from the relation $Kt = \text{constant}$, this would be equivalent to :

$$-\log t = \frac{A}{T} + B' \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Taking Table V. in Mr. Whiteley's paper as an example, the results have been plotted in this form (Fig. B) and they show that the expected straight-line relation between $\log t$ and $1/T$ is obtained.

It is clear that the laws controlling crystal growth are essentially similar to those controlling monomolecular reactions, so that progress and considerable simplification in our views on this subject can be expected from a more detailed theoretical study on this basis. To that end, the extensive and accurate data which Mr. Whiteley has given in this paper will be of the greatest assistance.

Mr. A. U. HUDDLE (Cambridge University) : This paper is of great interest to me, as it presents data indicating that the carbide form is one of the major factors in grain-size control. Many papers have been published on this subject, dealing with both pure and commercial alloys, but no satisfactory conclusions have been reached on the mechanism.

Of the grain-refining elements aluminium is undoubtedly the most important, but vanadium¹—and to a lesser extent silicon and manganese—can inhibit austenitic grain growth. It is well known that vanadium promotes spheroidisation and that its carbide is extremely difficult to dissolve in the austenite.¹ A small addition of either vanadium or aluminium (about 1%) is sufficient to suppress the γ -loop in alloys containing no carbon. These facts suggest that both elements will (a) increase the mobility of foreign atoms in the ferrite (*i.e.*, increase the rate of diffusion of solute atoms just below the Ac line), and (b) lower the solubility of carbon in austenite, giving smaller concentration gradients of carbon and therefore a slower rate of diffusion of carbon in austenite.

As the carbides of iron and manganese are isomorphous it seems reasonable to assume (as stated by the author) that manganese will replace iron in the carbide lattice (*cf.* equilibrium between

¹ J. G. Zimmermann, R. H. Aborn and E. C. Bain, *Transactions of the American Society for Metals*, 1937, vol. 25, pp. 755-787.

iron, manganese and sulphur). Some aluminium carbide may also be formed. Therefore, on entering the austenitic range we have (a) a carbide containing manganese, and possibly aluminium, which will probably be less soluble in austenite than cementite, and (b) an austenite, which, owing to the presence of aluminium, will be a poor solvent for the carbide. While this carbide, which is *crystallographically related* to the austenite lattice, remains undissolved, grain growth will be inhibited,¹ as each carbide particle will act as a stabiliser for each grain.

It has been shown that cementite (iron carbide) is readily dissolved in austenite, and this is one of the most important factors against the carbide theory. Now, if it is manganese carbide (perhaps aluminium as well) of which the rate of solution in austenite, at temperatures below about 1000° C., is slow (*cf.* vanadium carbide), then we can account for the conclusions of the workers² when using high-purity alloys low in manganese.

This gives us an explanation of the phenomenon known as "abnormality." If, at the moment of quenching, there is already a carbide nucleus favourably orientated to the austenite lattice, it will be impossible, under normal quenching conditions, to super-cool the austenite sufficiently to suppress the $\gamma \rightarrow \alpha$ transformation to below 200° C. (necessary for the formation of martensite), the relatively soft ferrite plus carbide being formed.

Dr. DAVID BINNIE (Lancashire Steel Corporation, Ltd., Irlam, near Manchester): I should like to ask a question relating to Section 8 of this paper. I notice that the author has carried out experiments on the diffusion of aluminium into solid steel. The method of using aluminium for grain-size control is, of course, to add it to the liquid steel, and I have always thought that the oxidation of aluminium under conditions which result in the separation of nuclei on freezing was essentially the cause of the resistance of the steel to grain growth. In the solid steel the oxide had already separated into a massive form, and I cannot see how the conditions then existed for the formation of nuclei.

Perhaps if oxygen were diffused into these aluminium-treated steels more positive evidence on the mechanism of grain-size control would be obtained.

Mr. G. BURNS (Admiralty Engineering Laboratory, Middlesex): With regard to the effect of the cooling rate from very high temperatures modifying the grain-growth characteristics, I take it that, in all cases, after heating to the high temperature the austenite

¹ H. W. McQuaid, *Transactions of the American Society for Metals*, 1935, vol. 23, pp. 797–838.

² G. R. Brophy and E. R. Parker, *Transactions of the American Society for Metals*, 1937, vol. 25, pp. 315–324.

G. Derge, A. R. Kommel and R. F. Mehl, *Transactions of the American Society for Metals*, 1938, vol. 26, pp. 153–172.

grain size was coarse. I have recently examined some flash butt-welds in $\frac{3}{4}$ -in. dia. bars, and there the material immediately adjoining the junction, which had been heated near to the solidus, remained fine-grained. The whole cycle of heating and soaking had taken only about 10 sec., insufficient time for the grain size to coarsen. Might a similar position arise with regard to the effect noted by Mr. Whiteley, that so rapid a heating and soaking cycle would diminish or eliminate the effect?

CORRESPONDENCE.

(Fig. C — Plate XLVIII.)

Mr. C. C. HODGSON (Leyland Motors, Ltd., Leyland) wrote: This paper is a valuable contribution to the literature on austenitic grain size, and, whilst it is not directly concerned with the grain-size rating of steel for commercial purposes, it is perhaps opportune to refer to the misconceptions that already exist, and are likely still further to develop, from the tendency to assign to the general term "grain size" the narrower meaning of an austenitic grain size produced under test conditions that are purely arbitrary. During the last few years a lot has been written on grain size in many sections of the technical press, and it is to be feared that many engineers are only imperfectly aware of the many factors which can influence it. If a condensed and simplified version of Mr. Whiteley's paper could be made available to engineers, it would undoubtedly do much to overcome some of the misconceptions which exist about the meaning of the terms "grain size" and "controlled grain size" at the present time.

If it is unfortunate that the practice of using the words "grain size" in this narrow sense is almost well established, it is still more unfortunate that one now sees the tendency to omit any mention of the imposed conditions under which the crystals were formed, for it is well known that it is by no means uncommon to vary those conditions according to the type of steel and the way in which it is to be used; and yet a recent official specification for medium-carbon steel simply stated "... this steel may be ordered ... to have ... a grain size 5/6." The size one assumes refers to the A.S.T.M. index number, and if it were a carburising steel one might be justified in assuming that the McQuaid-Ehn method was intended, using a temperature of 927° C., but this temperature is much higher than would be used in heat-treating the steel under discussion. Is it intended, therefore, to determine the austenitic grain size by normalising from, say, 843° C., a temperature that has been used for medium-carbon steel in American tests, or from somewhere, or anywhere, within the hardening range of 810–840° C. mentioned in the specification in reference to the heat treatment of the steel?

Turning more directly to the paper itself, the observation that

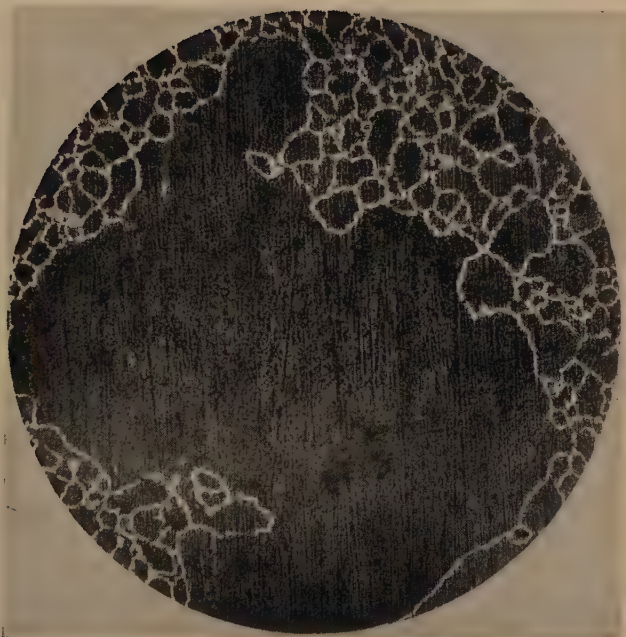


FIG. C.—Nickel-Chromium Case-Hardening Steel. McQuaid-Ehn test at 927° C. $\times 100$.
(See Hodgson's contribution).

[Correspondence on Whileley.
[To face p. 574 P.

the Ac_3 point is without significance on recrystallisation and can be ignored, whilst it may be true in the particular instance to which Mr. Whiteley refers, is ambiguous, and, taken out of its context, may be construed as meaning something quite different from what the author intended. Practical heat-treaters might interpret the statement as a negation of what they have always been taught and as meaning that it is not necessary to heat through the Ac_3 range when carrying out annealing or refining operations. There are a few applications where heating within the Ac_1 - Ac_3 interval can be applied to medium-carbon steel with advantage, but such treatment should follow a suitable refining treatment carried out at a temperature above the Ac_3 point.

It seems to me important that we should have more information on the factors controlling the tendency to dominant grain growth which some steels exhibit—growth of the type shown in Fig. 29 of the paper, for example—and it is to be hoped that Mr. Whiteley will find the time to pursue this aspect of the subject further. Dominant growth of this kind is not confined to medium-carbon steel or to the method of manufacture used by Mr. Whiteley. I have known specimens of nickel-chromium steel, made by the basic electric arc process, to show the effect after carburising at 927° C. for the McQuaid-Ehn test. In some instances grains which were too large to be included on the standard A.S.T.M. circle were developed in a steel which otherwise had an A.S.T.M. index number of 6 (Fig. C); with such a steel it is not always safe to use the simplified methods of processing permissible with a steel uniformly fine-grained under the same conditions.

The influence of previous thermal treatment or mechanical work on the grain size developed on subsequent heating makes one wonder whether some form of standardised preliminary heat treatment should be given before determining the austenitic grain size when using this as an acceptance test, for it is certain that often the forged tag-end or forged test bar is in a very different condition from that of the forging or drop forging that it represents.

AUTHOR'S REPLY.

MR. WHITELEY replied: I value greatly Dr. Desch's appreciative remarks and note that he refers to my use of small specimens. Except when an investigation necessitates it, I seldom take large specimens for microscopic work, since they increase many times the labour involved in obtaining a satisfactory surface. A small specimen can be prepared in about three minutes and with very little liability for surface flow to occur in the cloth polishing. It was, of course, absolutely essential in many of the grain-growth experiments to take specimens less than one gramme in weight when the

rate of heating was to be rapid. Dr. Desch says that I have shown how a coarse-grained steel can be changed by high-temperature treatment into one having similar properties to those of a fine-grained steel. That similarity does not necessarily include the physical properties, however, and in order to avoid any misunderstanding I should emphasise that throughout the investigation my attention was confined to grain-size effects as observed microscopically. I made no attempt to correlate changes in grain size with physical properties. Swinden and Bolsover¹ had already recorded some excellent work on that aspect of the subject, although it is now clear that more enquiry in that direction is needed. I doubt whether coarse-grained steels after a high-temperature treatment and subsequent refinement will show Izod values equal to those given by the same steels made fine-grained by the addition of aluminium. Dr. Desch seems to have got a wrong impression from his perusal of the last Section of the paper, for in the experiments there described I endeavoured to convert a coarse-grained steel into one that was fine-grained by diffusing aluminium into it when in the solid state. As unmistakable evidence that aluminium had so diffused was not forthcoming, I could form no definite conclusion as to the effect of that element in solid solution on grain growth. Dr. Desch also refers to the possibility that fine intergranular films have a determining influence on grain growth, as postulated by Benedicks.² It is one that I always kept in mind, but no indication of these films was to be seen. They were not revealed in quenched specimens by ordinary etching reagents, and, in the absence of any positive evidence of their existence, I found it difficult to visualise their behaviour as growth proceeds after the Ac_1 refinement. Do they become thicker as the area occupied by the grain boundaries diminishes with increasing grain size?

Dr. Swinden's favourable reception of the paper is particularly gratifying, since he must be regarded as an expert on the subject, but I cannot allow his statement that I was sceptical of some of the results which he and Mr. Bolsover presented in 1936 (*loc. cit.*) to pass without comment. In discussing that paper I accepted all their results as correct and from them merely endeavoured to indicate that the excellent physical properties shown by the fine-grained steels might not be due entirely to the grain size, since the physical properties of the coarse-grained steels which they had examined were much less satisfactory even when the grain sizes were apparently comparable with those of the fine-grained steels. Dr. Swinden mentions the McQuaid-Ehn carburising test for grain size, and I agree that it is a very useful one for distinguishing between coarse- and fine-grained hypo-eutectoid steels. But with mixed grain sizes

¹ T. Swinden and G. R. Bolsover, *Journal of The Iron and Steel Institute*, 1936, No. II., p. 457 P.

² C. Benedicks, *Journal of The Iron and Steel Institute*, 1937, No. I., p. 211 P.

I am not so certain, for, after carburisation, differences between the large and small grains are often considerably less than those revealed by the ferrite precipitation method. Unfortunately, the latter is only applicable to medium-carbon steels, and in that respect the carburising test undoubtedly has the advantage.

I consider that Dr. McCance has made a most valuable contribution to the discussion. Time and again during the investigation I felt that a mathematical treatment of the results might lead to an elucidation of the process of grain growth, but no method of approach suggested itself. Dr. McCance, with his keen mathematical insight, has indicated one. Lord Kelvin was in the habit of saying that "if you can measure that of which you speak, and can express it by a number, you know something of your subject; but if you cannot measure it your knowledge is meagre and unsatisfactory." Thus, Dr. McCance's ascertainment that the rate of grain growth in coarse-grained steels resembles that at which a monomolecular reaction progresses may prove very helpful in future work, notwithstanding that, in such reactions, one molecule may change into two or more, whereas in grain growth the reverse must happen, a single grain absorbing one or more.

Mr. Huddle has ably advanced the view that undissolved carbide has a controlling influence on grain growth. That the condition of the carbide is of great importance and can govern in large measure the extent of growth, even at temperatures above 1100° C., appeared repeatedly during the investigation. The theory that undissolved carbide can act as an inhibitor of grain growth is, however, open to the objection that it is difficult to see how any carbide can remain undissolved during long periods of heating at temperatures well above the critical range and *yet* the grain size may remain very small. It may be that aluminium as well as vanadium makes the carbide more resistant to solution at temperatures immediately above that range, but there is at present little or no evidence of any such action. Moreover, it should be noted in this connection that American investigators have stated that aluminium ceases to be effective in grain-size control when added in too large a quantity.

Dr. Binnie has missed the point of the experiments described in Section 8. My aim there was to produce a fine-grained steel by introducing aluminium under conditions in which alumina particles would presumably not be formed, but I could not regard the results as conclusive. To my mind, one of the chief objections to the inclusion-nuclei theory as propounded by Bain and others is that the change to a fine-grained steel does not begin apparently until after the aluminium has combined with all the oxygen in the steel. In other words, an excess of aluminium above that required for combination with the oxygen seems to be needed to produce a fine-grained steel.

Mr. Burns is quite correct in his assumption that, in all cases,

the grain sizes of the coarse-grained steels were very large after their treatment at temperatures between 1200° and 1400° C. as described in Section 6. Yet, notwithstanding their large initial grain size, those pieces which had been soaked at between 1350° and 1400° C. gave a small grain size when heated for several hours at 930° C., provided that they had been air-cooled from the high temperature. Moreover, this halt in growth so characteristic of fine-grained steels was still in evidence after the pieces had been refined, as I have indicated in Table XXVIII. With regard to flash butt-welding mentioned by Mr. Burns, I recently examined a piece of coarse-grained medium-carbon steel of about 1 in. square section which had been so welded, and found that when a section taken across the weld was heated for 2 hr. at 930° C. the grain size remained small in the immediate vicinity of the fused zone but quickly became large as the distance from the actual weld increased. That could, no doubt, be accounted for by the steep temperature gradient to below 1200° C. which would exist during the welding operation.

Mr. Hodgson raises the question of grain-size specifications. In my experience it is the intermediate sizes which are the most troublesome to obtain with any degree of certainty. Generally, when an attempt is made to produce a steel with a No. 5 size, for instance, by reducing the aluminium addition, a mixed grain size appears in the carburising test at 930° C. That is not the case at 850° C., however, for, even after long periods of heating at and near that temperature, the grain sizes of such steels as revealed by the ferrite precipitation method are usually as small as those given at 930° C. by really fine-grained steels. Yet the Izod values of the mixed-grain-size steels after quenching at about 850° C. and tempering are as a rule decidedly lower than those of similarly treated steels which are unmistakeably fine-grained. Mr. Hodgson takes me to task for the observation that the Ac_3 point is without significance in grain-growth investigations. In so doing I am not sure that he is justified, for it is distinctly indicated in the paper that a complete refinement necessitates a passage right through the critical range in order to eliminate the whole of the hypo-eutectoid ferrite and more than one passage to counteract the effect of a large initial grain size. In the thermal refinement of the coarse-grained steels two heatings were always given at 850° C., as is stated on p. 530 P. Mr. Hodgson's illustration of what appears to be abnormal growth, as I have termed it, which occurred in a nickel-chromium steel when subjected to the McQuaid-Ehn test is both striking and instructive, for I have not so far encountered that mode of development during carburisation. When using the ferrite precipitation method, abnormal growth seemed to begin at a lower temperature after a rapid heating and also in pieces which had been refined mechanically. It would, therefore, be of interest to know whether Mr. Hodgson's specimen was taken from a forged piece.

THE PHYSICAL CHEMISTRY OF OPEN-HEARTH SLAGS.*

BY JAMES WHITE, D.Sc., Ph.D., A.R.T.C. (THE ROYAL TECHNICAL COLLEGE, GLASGOW).

SUMMARY.

The principal oxides occurring in open-hearth slags are CaO , MgO , MnO , FeO , Fe_2O_3 , Al_2O_3 , P_2O_5 and SiO_2 , and a knowledge of the systems formed by these oxides with each other is essential to an understanding of the nature of the slag and of its rôle in steel-making. In the present paper the available data concerning these systems are discussed and correlated, thermal equilibrium and phase diagrams are given where these are available, and probable forms of some of the as yet unknown diagrams are suggested on the basis of published information. Particular attention is paid to the equilibria governing the relationships between the oxides of iron and gaseous oxygen on the one hand, and between these oxides and metallic iron on the other. The modifying effects produced by the presence of other oxides on these relationships are also discussed under the headings of the appropriate systems. Hence, the mechanism of gas oxidation in the furnace is briefly discussed.

On the basis of the data thus presented the question of the constitution of actual furnace slags is discussed, and a tentative scheme of phase assemblages in solidified basic slags is put forward, which, it is hoped, may serve as a basis (to be proved or amended) for further work on the subject. Fusibility and fluidity relationships in furnace slags are also considered in so far as they limit the range of "workable" compositions.

Finally the question of the molecular constitution of liquid slags is briefly discussed.

I.—INTRODUCTION.

IN this paper a survey is made of our present knowledge of the fundamental physico-chemical relationships governing the constitution and properties of open-hearth slags. Its purpose is twofold—first, since progress in this field has been somewhat rapid in recent years, it was thought that an attempt to review and correlate the information now available might be desirable, and, secondly, since the knowledge dealt with is scattered widely in the form of original papers throughout many different scientific journals, it was considered that it would be of service to those interested in the subject to bring together this material in a readily accessible form. For this reason a good many diagrams, particularly constitutional and thermal equilibrium diagrams, have been reproduced.

As regards its scope, the paper is concerned primarily with the chemistry of the slag, and so no attempt (other than incidental) has been made to consider the relationships involved from the point

* Received December 23, 1942.

of view of their influence on the metal bath. This aspect of the steelmaking process has been adequately dealt with by others, notably by McCance⁽¹⁾ as recently as 1938 in the Symposium on Steelmaking of The Iron and Steel Institute.

II.—THE GEOPHYSICAL TEMPERATURE SCALE.

Throughout this paper the symbol “#” appended to a diagram (or to temperatures over 1100°C. mentioned in the text) signifies that the temperatures quoted are given in terms of the temperature scale of Day and Sosman.⁽¹⁷¹⁾ Temperatures on this scale were fixed on the basis of determinations up to 1500°C. with a nitrogen-filled gas thermometer, corrections for deviations from the gas laws being applied. This scale was adopted by the workers of the Geophysical Laboratory, Washington, where it was established. They used it to correct all temperatures determined in that laboratory prior to 1911, and have continued to use it ever since. The International Temperature Scale, however, over its high-temperature range, is now based on the determination of standard temperatures by methods utilising radiation measurements, and differs appreciably at high temperatures from the Geophysical Scale, *e.g.*, the melting point of palladium is taken as 1555°C. and that of platinum as 1773°C. , as against 1549.2°C. and 1755°C. on the Geophysical Scale. Corrections must, therefore, be made to temperatures determined in the Geophysical Laboratory when direct comparison with the work of laboratories using the International Scale is desired. Tables of such corrections have been given by Wensel and Roeser⁽¹⁷²⁾ and by Sosman.⁽¹⁷³⁾ According to the latter these are 0° at 1100°C. , $+1^{\circ}$ at 1200°C. , $+1^{\circ}$ at 1300°C. , $+2^{\circ}$ at 1400°C. , $+3^{\circ}$ at 1500°C. , $+6^{\circ}$ at 1600°C. , $+15^{\circ}$ at 1700°C. and $+20^{\circ}$ at 1800°C. Thus the melting point of SiO_2 (cristobalite), which was first determined by Ferguson and Merwin⁽¹⁷⁴⁾ to be $1710 \pm 10^{\circ}\text{C.}$ and later redetermined by Greig⁽¹⁰⁾ to be $1713 \pm 5^{\circ}\text{C.}$, was given by Sosman, after application of a correction of $+15^{\circ}\text{C.}$, as 1728°C. Such corrections cannot, however, be legitimately applied to determinations by other workers, *e.g.*, the melting points of CaO , Al_2O_3 and MgO determined by Kanolt⁽¹⁷⁵⁾ cannot be so corrected. An attempt to give corrections supposedly of general applicability to the high-temperature range in which these lie⁽¹⁷⁶⁾ has been strongly criticised by Wensel.⁽¹⁷⁷⁾ Hence, for these oxides the original melting points given by Kanolt are used throughout this paper.

III.—THE PRINCIPAL CONSTITUENTS OF OPEN-HEARTH SLAGS.

The open-hearth slag is derived principally from the oxidation of the charge, from the addition of slag-forming materials to the furnace and from the attack of the charge on the hearth refractory. The substances which thus find their way into the slag layer are

chiefly SiO_2 , FeO , MnO , CaO and MgO in the acid process, and CaO , FeO , MnO , MgO , SiO_2 , P_2O_5 and Fe_2O_3 in the basic process. In addition, both types of slag generally contain 2–3% of Al_2O_3 . Slag chemistry is, therefore, concerned essentially with the relationships prevailing within systems of these oxides.

IV.—THERMAL EQUILIBRIUM DIAGRAMS OF THE SLAG-FORMING OXIDES.

The elucidation of the thermal equilibrium diagrams of systems of the slag-forming oxides has played an important part in the study of slags. In addition to providing extremely useful information on the relationships between the melting points of slags and their compositions, such diagrams give fundamental data on slag constitution. Such studies, supplemented by the results of the petrographic examination of solidified furnace slags, form the basis of our knowledge of the chemical constitution of slags, and the relationships observed have been widely used to explain the reactions of steelmaking. It should be realised, however, that the constitutional relationships so established are the result of conditions prevailing at and below the freezing point of the slags, and are not necessarily the same as those holding in the liquid slag at steel-making temperatures, and that the separation of a crystalline compound on freezing is not necessarily proof that the compound existed in the liquid state. Again, the number of crystalline constituents separating from a liquid slag on freezing is subject to the limitations imposed by the phase rule, whereas no such limitations apply to the number of molecular species that may be present in solution in each other in the liquid slag. Furthermore, the equilibrium relationships in the solid state are largely determined by structural as well as by purely chemical considerations, and the presence, or absence, of isomorphism in the phases capable of crystallising out may affect the constitution considerably. In the liquid state no such influences are likely to be operative, though the existence of true double salts in solution may be possible. Nevertheless, in spite of these differences between the two states, it is a fact that a knowledge of the physico-chemical relationships prevailing within solid slags has contributed materially towards a better understanding of the behaviour of liquid slags in the furnace, and it must, therefore, be concluded that the chemical constitution of the liquid slag is not entirely unrelated to that of the solid slag.

In recent years knowledge of the thermal equilibrium diagrams of the systems formed by the slag-forming oxides has been considerably increased. This is well illustrated by the fact that almost all of the diagrams given by Benedicks and Löfquist in 1930 in their book "Non-Metallic Inclusions in Iron and Steel"⁽²⁾ have since undergone considerable revision in the light of later researches. Most of the more important binary and ternary systems of the slag-

forming oxides have now been investigated and their diagrams are known at least in part. There are, of course, considerable difficulties in representing relationships in systems containing more than three, or at the most four, components, and, further, the amount of work required to investigate such multi-component systems adequately is very great. It is not generally possible, therefore, to represent completely the constitutional relationships of actual furnace slags on a single diagram, owing to their complexity. Nevertheless, valuable information is obtained by considering these slags in the light of our knowledge of the simpler binary and ternary diagrams of their component oxides.

(a) *Basic Oxide Systems.*

Of the six binary systems formed by the oxides CaO, MgO, MnO and FeO with each other only four appear to have been investigated to any extent. Of these, the system CaO-MgO is eutectiferous with no appreciable solid solubility between the oxides, FeO-MgO and FeO-MnO form solid solutions, while CaO-FeO is not a true binary system, since mixtures of these oxides form phases the compositions of which can be represented only in terms of the ternary system CaO-Fe-Fe₂O₃. It is not proposed to discuss these systems at this stage, as this is done later under the headings of higher systems in which they occur. Concerning systems of higher order than binary formed by these basic oxides alone there is little direct information, but it seems likely that FeO, MnO and MgO will form extensive ternary solid solutions. Between these and CaO, however, solubility is likely to be somewhat limited.

(b) *Binary Systems of SiO₂ with the Basic Oxides.*

In Fig. 1 # are shown the thermal equilibrium diagrams of the four systems (A) FeO-SiO₂,⁽³⁻⁶⁾ (B) MnO-SiO₂,⁽⁷⁾ (C) CaO-SiO₂,⁽⁸⁻¹²⁾ and (D) MgO-SiO₂.^(13, 14, 10) A characteristic feature of all of these systems is the ability of the basic oxide to form one or more silicates with the acid oxide. CaO, the metal ion of which is the largest and most strongly electro-positive of the four, forms no fewer than four silicates, including the ortho- and meta-silicates (2CaO.SiO₂ and CaO.SiO₂), while MgO and MnO form ortho- and meta-silicates only. It is generally accepted now that FeO forms only an orthosilicate, though some of the earlier diagrams showed also the occurrence of the metasilicate. Later work^(3, 6) showed, however, that this compound did not crystallise from FeO-SiO₂ melts, and that the annealing of a glass of the composition FeO.SiO₂ at as low a temperature as 660° C. resulted in the crystallisation merely of the orthosilicate, fayalite, no evidence of the formation of the metasilicate being obtained.⁽³⁾ These findings were somewhat unexpected, since metasilicates approaching FeO.SiO₂ in composition were already known to mineralogists, and the name ferrosilite had been proposed for the pure end-member of the solid-solution series to

which it was considered that these metasilicates belonged. Later work showed, however (see sub-section (c) following), that, though certain metasilicates were capable of forming solid solutions in which up to 70–80% of the basic oxide was replaced by FeO, in no

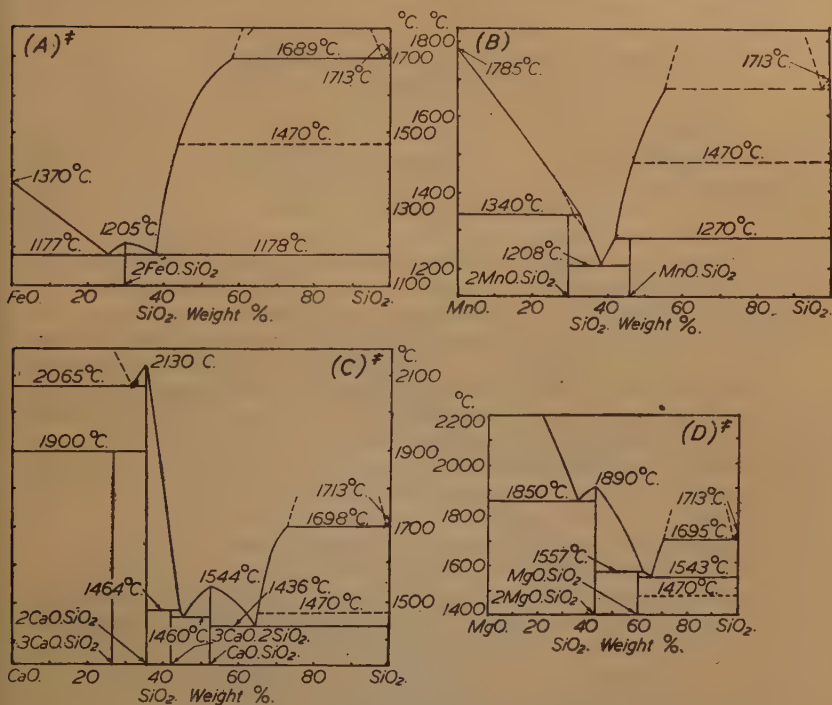


FIG. 1.—Thermal Equilibrium Diagrams of Basic-Oxide/Silica Binary Systems. (A) FeO-SiO₂ # (Bowen and Schairer,⁽³⁾ Greig,⁽⁴⁾ Hay, Howat and White⁽⁵⁾). (B) MnO-SiO₂ (White, Howat and Hay⁽⁷⁾). Tungsten-molybdenum thermocouple calibrated against melting point of Armeo iron taken as 1530° C. MnO melting point based on extrapolation of calibration curve. Correction of liquidus line near its intersection with tephroite peritectic horizontal necessary on theoretical grounds. Form indicated by broken line permissible. (C) CaO-SiO₂ # (Day, Shepherd and Wright,⁽⁸⁾ Rankin and Wright,⁽⁹⁾ Greig,⁽¹⁰⁾ Ferguson and Merwin,⁽¹¹⁾ Bowen, Schairer and Posnjak⁽¹²⁾). Revised temperatures quoted recently by Schairer (see note to Fig. 11(D)). (D) MgO-SiO₂ # (Bowen and Andersen,⁽¹³⁾ Bowen,⁽¹⁴⁾ Greig⁽¹⁰⁾).

case did the solubility extend to the pure end-member FeO.SiO₂, at least not in the synthetic melts studied. This, of course, confirmed the observations made on the binary system FeO-SiO₂. Still more recently, however, the position has been somewhat modified by Bowen,⁽¹⁵⁾ who has reported the discovery of minute crystals of the

monoclinic form of ferrosilite in an obsidian. Two possibilities are suggested : Either that it may have formed metastably, or that it may form stably and, presumably, very sluggishly, at temperatures below those previously investigated in the laboratory. As it has been found impossible to prepare it synthetically either from liquid melts or otherwise, it is not to be expected that it will occur in slags.

(It may also be noted that the amphibole grunerite, which has been considered by some writers to be essentially a metasilicate of iron approaching $\text{FeO} \cdot \text{SiO}_2$ in composition, actually contains a definite proportion of water (1 mol of H_2O to 8 mols of SiO_2), the hydrogen ions of which are apparently essential to, and occupy definite places in, the amphibole structure.⁽¹⁶⁾ Besides this, most natural grunerites contain quite appreciable amounts of MgO and MnO .)

All four diagrams, which are otherwise of the normal eutectiferous type with compounds, are characterised by the occurrence of a range of immiscibility in the liquid state at high silica contents due to the fact that liquid silica and the liquid silicates concerned are only partially soluble in each other. This is an important feature of these diagrams, since it causes the liquidus to rise steeply in each case to the monotectic horizontal, thus considerably restricting the solubility of solid SiO_2 in the liquid silicates at all temperatures below the monotectic temperature. Incidentally, the fluxing powers of the basic oxides for solid SiO_2 vary inversely as the distance of this portion of the liquidus from the SiO_2 end of the diagram. The tridymite-cristobalite transformation temperature is indicated on each diagram by a horizontal broken line at 1470°C .

It should be pointed out at this stage that the system $\text{FeO}-\text{SiO}_2$ is not, strictly speaking, a true binary system, since it is probable that FeO (or wüstite) undergoes peritectic dissociation on melting, with the liberation of free iron and the formation of a liquid containing ferric oxide (see Section V. below). Hence, all "binary" systems of which FeO is a component should strictly be considered as ternaries, while "ternaries" should be considered as quaternaries, and so on. For simplicity it is convenient to neglect this, however, when discussing the slag only, and to consider the FeO as a stable component.

(c) Ternary Systems of SiO_2 with Two Basic Oxides.

With SiO_2 the four basic oxides can be combined to form six different ternary systems. One of the most significant and characteristic features of these systems is the formation of solid solutions by replacement of the basic oxides by one another along the orthosilicate and metasilicate joins of the phase diagrams. The necessary conditions for solid solution formation of this type are : (1) that the crystal structures of the pure end-members of the series should be similar, and (2) that the sizes of the substituted and substituent ions should not differ too widely. Both these require-

ments are geometrical rather than chemical, though the charges on the ions involved are, of course, significant in that the structure as a whole must be electrically neutral. An illustration of the importance of these requirements is provided by the fact that MgO and FeO , which both have the NaCl type of cubic structure, and in which the radii of the metal ions are 0.78 \AA. and 0.83 \AA. respectively (*i.e.*, differing by only 6.4% of the smaller), are apparently completely soluble in each other, while CaO , which has the same type of structure but in which the radius of the Ca ion is 1.06 \AA. (*i.e.*, approximately 36% greater than that of the Mg ion and 28% greater than that of the Fe ion), gives apparently little or no solid-solution formation with either of these oxides. Again, in the spinel group of minerals MgO , FeO and MnO are extensively replaceable by one another (as are also the trivalent oxides), while CaO , on the other hand, forms aluminates and ferrites, which differ structurally from the spinels, and have, apparently, no appreciable solubility in them. Incidentally, these lime compounds are considerably more fusible than the spinels, a point which is of considerable importance to the basic-refractories technologist.

In the silicate systems at present under consideration the orthosilicates fayalite ($2\text{FeO} \cdot \text{SiO}_2$), tephroite ($2\text{MnO} \cdot \text{SiO}_2$) and forsterite ($2\text{MgO} \cdot \text{SiO}_2$), which are all orthorhombic and belong to the olivine group of minerals, appear to be truly isomorphous and completely soluble in each other in all proportions. The relationships between these and the corresponding lime compound, $2\text{CaO} \cdot \text{SiO}_2$, are complicated by the fact that the latter can exist in three allotropic modifications, α , β and γ , the change from α to β occurring at 1420° C. on cooling, and that from β to γ at 674° C. According to Day, Shepherd and Wright⁽⁸⁾ the β form is possibly orthorhombic, but more recently Bowen, Schairer and Posnjak⁽¹⁷⁾ have suggested that the γ form may be orthorhombic. Even so, the evidence available suggests that in none of its forms does $2\text{CaO} \cdot \text{SiO}_2$ form complete solid-solution series with the other orthosilicates. (Incidentally, the change from the β to the γ form is accompanied by a 10% increase in volume, and gives rise to the phenomenon of "falling" or "dusting," which occurs on cooling slags containing sufficient amounts of this material. As might be expected, the γ is the commonest natural form, though the mineral larnite, which Bowen, Schairer and Posnjak⁽¹⁷⁾ consider to be most probably the α form, is known.) Of the metasilicates, which all belong to the pyroxene group of minerals, rhodonite ($\text{MnO} \cdot \text{SiO}_2$) is triclinic, $\text{MgO} \cdot \text{SiO}_2$ exists as monoclinic clino-enstatite at high temperatures, but transforms to the orthorhombic form, enstatite, on cooling below 1145° C. , while $\text{CaO} \cdot \text{SiO}_2$ exists as monoclinic pseudowollastonite, or $\alpha\text{-CaO} \cdot \text{SiO}_2$, above 1150° C. ,^{(12)*} and as triclinic wollastonite, or $\beta\text{-CaO} \cdot \text{SiO}_2$, below that temperature. (A third

* Osborn and Schairer⁽¹⁷⁹⁾ have recently redetermined the inversion temperature of wollastonite at $1125 \pm 10^\circ \text{ C.}$

form of $\text{CaO} \cdot \text{SiO}_2$ designated as parawollastonite has also been suggested.⁽¹⁸⁾ The relationships between these minerals as regards solid-solution formation are thus exceedingly complex, and three pyroxene series, monoclinic, triclinic and orthorhombic, appear to

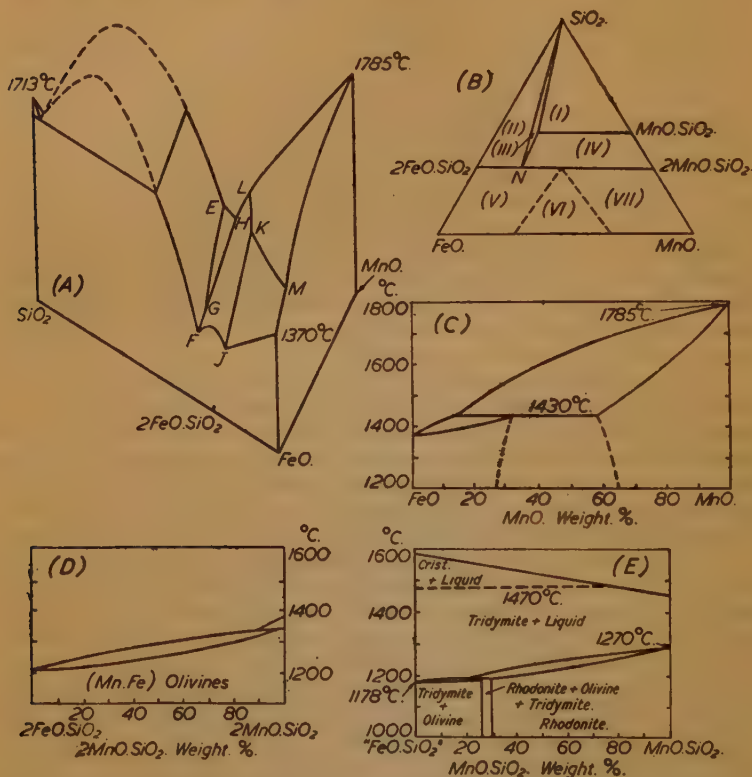
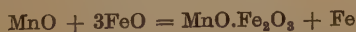


FIG. 2.—System FeO-MnO-SiO₂. (A) Liquidus surface (Hay, White and McIntosh⁽¹⁹⁾). (B) Phase distribution. Phase fields: (i) SiO₂ and rhodonite, (ii) SiO₂ and olivines, (iii) SiO₂, olivine and rhodonite, (iv) rhodonite and olivines, (v) olivines and FeO-MnO solid solutions, (vi) olivine, FeO-MnO solid solution and MnO-FeO solid solution, (vii) olivines and MnO-FeO solid solutions. (C) System FeO-MnO (Hay, Howat and White⁽⁶⁾). (D) 2FeO.SiO₂-2MnO.SiO₂ join (tentative). (E) "FeO.SiO₂"-MnO.SiO₂ join (tentative).

exist. Although the compound $\text{FeO} \cdot \text{SiO}_2$ does not separate from pure $\text{FeO} \cdot \text{SiO}_2$ melts, replacement of the bulk of the basic oxide in the three other metasilicates by FeO is possible, the resulting solid solutions being, in effect, solid solutions of $\text{FeO} \cdot \text{SiO}_2$ in these metasilicates. In each case, however, the homogeneity range of the

solid solution, at least as determined in synthetic melts, stops short of the actual composition $\text{FeO} \cdot \text{SiO}_2$. The discovery of ferrosilite, as mentioned above, raises doubts as to whether this can be considered as a true equilibrium condition.

Fig. 2 indicates (qualitatively in part) the phase and thermal relationships within the system FeO-MnO-SiO_2 .⁽¹⁹⁾ Fig. 2(A) shows the form of the liquidus surface, and Fig. 2(B) the phase distribution. Fig. 2(C) is the thermal equilibrium diagram of the binary system FeO-MnO as given by Hay, Howat and White;⁽⁶⁾ only partial solubility between FeO and MnO is indicated, and the diagram is of the same form as that suggested earlier by Benedicks and Löfquist⁽²⁾ on the basis of the data then available. On the other hand, diagrams showing complete solid solubility have been proposed by Andrew, Maddocks and Howat⁽²⁰⁾ and by Herty,⁽²¹⁾ though that of the former authors is probably suspect on the ground that melting was carried out in alumina crucibles, which would flux considerably with the melts, as is indicated by the fact that the melting point determined for pure MnO was much too low. More recently, however, Whiteley⁽²²⁾ failed to find any evidence of immiscibility in examining a series of artificially-produced FeO-MnO inclusions in steel. The diagram of Hay, Howat and White was based on evidence obtained from thermal data and microscopic examination of the powdered melts, and no examination of the actual structures obtained was made. Since then, however, the structures of a few melts within the suggested immiscibility range have been examined and the existence of two phases apparently confirmed.* The evidence regarding the mutual solubility of FeO and MnO is, therefore, conflicting. It is possible, however, that the appearance of a two-phase range in the series might result if the Fe_2O_3 content of the " FeO " used were abnormally large, resulting in the formation of a certain amount of $(\text{Mn,Fe})_3\text{O}_4$ solid solution along with the MnO-FeO solid solution (see Fig. 20(A)). A measure of support is lent to this suggestion by the fact that Whiteley's inclusions, having frozen in contact with metallic iron, would presumably contain a minimum of Fe_2O_3 . An alternative possibility, that MnO acts on FeO in a manner similar to that of CaO (see discussion of Fig. 19(A), Section VI.(b) below), can probably be dismissed, as the compound which would be formed in this case, viz., $\text{MnO} \cdot \text{Fe}_2\text{O}_3$, has a high dissociation pressure† and could not exist in contact with metallic iron. In other words, the reaction



will go from right to left, not from left to right.

For the present, the existence of an immiscibility zone in the FeO-MnO series of solid solutions has been accepted, and the

* Carried out at the Royal Technical College, Glasgow. Unpublished.

† See Section VI. below.

diagrams of later systems in which these two oxides occur have been drawn on this assumption. The differences between the two alternative forms of diagram will be of a minor character in most cases.

In the ternary diagram the complete solid-solution series from fayalite to tephroite gives rise to a rather flat ridge on the liquidus surface, as shown in Fig. 2(A). The mineral knebelite is a member of this series, containing approximately equimolecular amounts of the two silicates. It is uncertain whether it is to be regarded as a definite compound or not. Assuming that it is not, the probable form of the section fayalite-tephroite is as shown in Fig. 2(D). This is not a true binary section, since tephroite melts incongruently. The metasilicate solid-solution series extends from rhodonite towards the composition $\text{FeO} \cdot \text{SiO}_2$. Owing to the non-existence of $\text{FeO} \cdot \text{SiO}_2$ and the incongruent melting of rhodonite, the section along the metasilicate join will not be a binary one either. Its probable form, assuming that the point *G* of Fig. 2(A) is a reaction point, not a ternary eutectic, is shown in Fig. 2(E). The limit of the rhodonite homogeneity range is based on the findings of Whiteley and Hallimond,⁽²³⁾ who found that rhodonite appeared in acid-furnace slags low in lime when the ratio of MnO to FeO exceeded 27/73 approximately, the ratio in the resulting rhodonite being 29/71. The latter ratio was used to fix the limit of the homogeneity range, and the former to fix the position of the point *N* of Fig. 2(B). It is probable that no great accuracy can be claimed in either case, however. For one thing, CaO of the order of 5% was present in the "iron rhodonites" of Whiteley and Hallimond. Further, later studies on these iron rhodonites have shown⁽²⁴⁾ that they differ structurally from natural rhodonite, but that they resemble instead the minerals pyroxmangite and sobralite, naturally-occurring mixed metasilicates of FeO, MnO and CaO low in CaO. On the other hand, Sundius⁽²⁵⁾ has reported the occurrence of a true iron rhodonite, isomorphous with rhodonite. It would appear, therefore, that two distinct series may occur, though how they are related, whether as enantiotropes or otherwise, it is not yet possible to say. It seems likely, however, that the relationships shown in Fig. 2(E) will be too simple, but a more detailed investigation of the system FeO-MnO-SiO_2 , particularly with regard to possible inversions in the solid state, will be necessary before a final conclusion can be reached.

Owing to the extent of the solid-solution formation, the form of the ternary diagram (Fig. 2(A)) is relatively simple. Two eutectic troughs, *FGH* and *JKL*, the latter of which merges into the trace of the tephroite peritectic, cross the diagram approximately parallel to the direction of the solid-solution series. Both *G* and *K* appear to be reaction points, not ternary eutectics, and hence the fusion surfaces slope continuously towards the FeO-SiO_2 side of the diagram, though the slope from *H* to *F* is but slight. From *FH*

the liquidus surface rises steeply with increasing SiO_2 till it meets the plane underlying the biliquidal zone (which plane joins the biliquidal horizontals of the two binary silicate systems). The position and shape of the liquidus surface in this region are such that at 1600°C . the SiO_2 content of a SiO_2 -saturated slag is approximately 50% and is probably little affected by variations in the ratio of the FeO to MnO .⁽²⁶⁾ If anything, it may increase by a few per cent. as the proportion of MnO is increased.

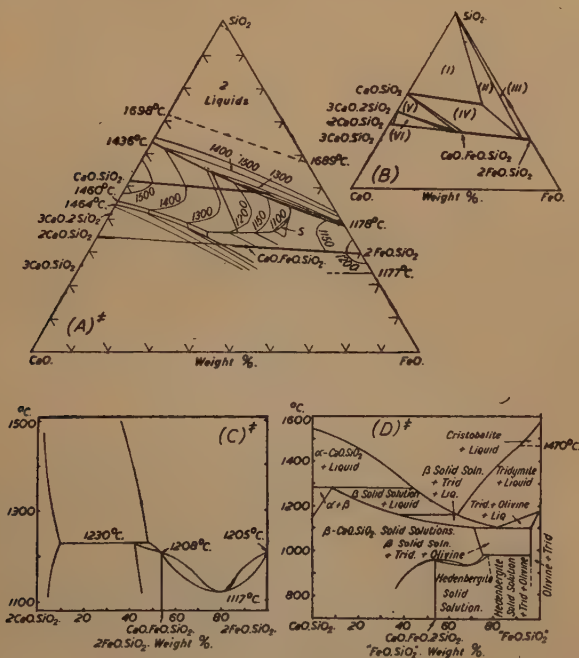


FIG. 3.—System CaO-FeO-SiO_2 #. (A) Liquidus surface (Bowen, Schairer and Posnjak⁽¹²⁾). Temperatures along CaO-SiO_2 edge according to Schairer (see note to Fig. 11(D)). (B) Phase distribution at 1090°C . Phase fields: (i) SiO_2 and wollastonites, (ii) SiO_2 , FeO -saturated wollastonite and olivine, (iii) SiO_2 and olivines, (iv) wollastonites and olivines, (v) wollastonite, 3CaO.2SiO_2 and olivine, (vi) 3CaO.2SiO_2 , 2CaO.SiO_2 and olivine. (C) 2CaO.SiO_2 - 2FeO.SiO_2 join (Bowen, Schairer and Posnjak⁽¹⁷⁾). (D) CaO.SiO_2 -“ FeO.SiO_2 ” join (Bowen, Schairer and Posnjak⁽¹²⁾).

Details of the system CaO-FeO-SiO_2 according to Bowen, Schairer and Posnjak^(17, 12) are given in Figs. 3#, 3(A) and 3(B) showing the ternary diagram, and 3(C) and 3(D) the orthosilicate and metasilicate joins, along both of which there is again extensive solid solubility, though in neither case is it complete—at least at the temperatures covered by the diagrams. In Fig. 3(C) the tempera-

tures covered are such that $2\text{CaO} \cdot \text{SiO}_2$ occurs in the β form. The system is too sluggish at low temperatures to allow the solubilities in the γ form to be measured, but Bowen, Schairer and Posnjak consider it unlikely that there is complete solubility in this form either, though it is probably somewhat higher than in the β form.⁽¹⁷⁾ A compound $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$ (iron monticellite or calcium olivine) of definite melting point, and isomorphous with fayalite, occurs in this series. The metasilicate join ($\text{CaO} \cdot \text{SiO}_2$ —"FeO.SiO₂"') is again pseudo-binary. As shown in Fig. 3(D), no solubility in monoclinic α - $\text{CaO} \cdot \text{SiO}_2$ has been found, but in the triclinic β form the solubility extends to a composition corresponding to approximately 75% of "FeO.SiO₂" at 960° C. At lower temperatures, however, solubility in the triclinic form is more restricted, owing to a breakdown in the more "FeO.SiO₂"-rich solutions on cooling to form a monoclinic series which includes the mineral hedenbergite ($\text{CaFeSi}_2\text{O}_6$) and which extends to a composition corresponding to roughly 80% "FeO.SiO₂." The minimum in the liquidus of Fig. 3(D) is due to the fact that the upper eutectic trough of Fig. 3(A) crosses the metasilicate join. In the complete ternary system there are no fewer than seven invariant points, but no ternary eutectic point occurs. The point *S* is, however, a minimum point and represents the lowest melting temperature (1093° C.) of the system. The general form of the liquidus surface is shown by the isotherms of Fig. 3(A). The width of the biliquidal zone decreases progressively from the FeO-SiO₂ binary to the CaO-SiO₂ binary, the limit of the zone running roughly parallel to the upper eutectic trough. Because of this, the SiO₂ content at saturation of CaO-FeO-SiO₂ slags below the temperature of immiscible-liquid formation increases progressively as the ratio of CaO to FeO increases. In addition to the two ternary compounds already mentioned, a third one, $2\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$ (ferrous akermanite), occurs on the binary join between $\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$, but it is stable at low temperatures only and dissociates in the solid state on heating to 775° C. The presence of other substances in solid solution, such as, for instance, the analogous but more stable mineral akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), probably raises the decomposition temperature, and a mineral corresponding to approximately 80% of ferrous akermanite has been reported in a slag.⁽¹²⁾

In the system MgO-FeO-SiO_2 ⁽²⁷⁾ (Fig. 4#) there are three extensive solid-solution series, namely, the MgO-FeO series of cubic magnesio-wüstites (Fig. 4(C)), the orthosilicate fayalite-forsterite series of orthorhombic olivines (Fig. 4(D)), to which most of the natural olivines, *e.g.*, chrysolite, essentially belong, and the metasilicate series extending from $\text{MgO} \cdot \text{SiO}_2$ to a composition corresponding to 87% of "FeO.SiO₂" (Fig. 4(E)). It is noteworthy that only the central composition range of this latter series melts congruently. To the left of this range incongruent melting with separation of olivine takes place, as in the case of $\text{MgO} \cdot \text{SiO}_2$ itself,

while to the right of it tridymite separates on melting. The minimum in the liquidus is caused by the upper eutectic trough of Fig. 4(A) crossing the join. The relationships involved are made

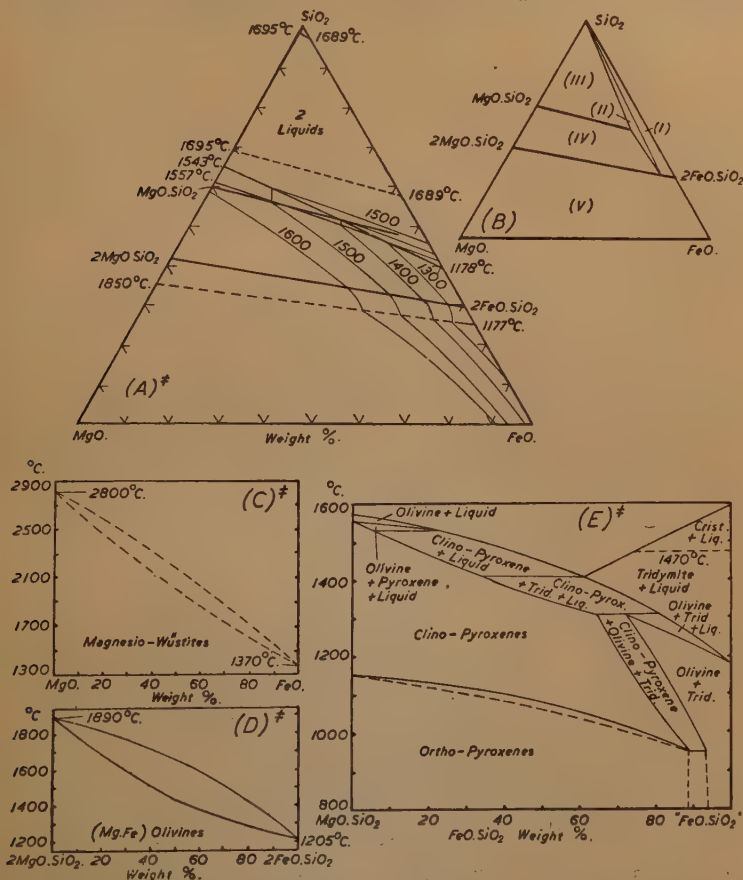


FIG. 4.—System MgO-FeO-SiO₂. (A) Liquidus surface (Bowen and Schairer⁽²⁷⁾). (B) Phase distribution at 1170° C. Phase fields: (i) SiO₂ and olivine, (ii) SiO₂, FeO-saturated clino-pyroxene and olivine, (iii) SiO₂ and clino-pyroxenes, (iv) clino-pyroxenes and olivines, (v) olivines and magnesio-wüstites. (C) Probable form of thermal equilibrium diagram of system MgO-FeO (Bowen and Schairer⁽²⁷⁾). (D) 2MgO.SiO₂-2FeO.SiO₂ join (Bowen and Schairer⁽²⁷⁾). (E) MgO.SiO₂-FeO.SiO₂ join (Bowen and Schairer⁽²⁷⁾).

clear in the ternary diagram, Fig. 4(A). The transformation that occurs at 1145° C. in enstatite, Fig. 4(E), persists over the entire solid-solution range, the monoclinic pyroxenes stable at high temperatures transforming on cooling to the orthorhombic form.

Like most transformations in the solid state, however, the change-over tends to be sluggish, and, with some members of the series at least, very slow rates of cooling would be necessary for it to proceed to completion. Owing to the extent to which solid solutions form, the number of fields and field boundaries in Fig. 4(A) is almost a minimum. There are two binary eutectic troughs as shown, and there is no ternary eutectic. Hence, the lowest melting points are all on the FeO-SiO₂ side of the diagram. As in the two previous systems, the biliquidal zone stretches across the high-silica region of the diagram, decreasing in width somewhat as the MgO-SiO₂ binary is approached. MgO, like CaO, therefore, increases the solvent power of ferrous slags for silica, though it is not quite so powerful in this respect as the latter oxide.

The system CaO-MgO-SiO₂^(11, 10, 28) is of considerable complexity, and no fewer than four ternary compounds—CaO.MgO.2SiO₂ (diopside), CaO.MgO.SiO₂ (monticellite), 2CaO.MgO.2SiO₂ (akermanite) and 5CaO.2MgO.6SiO₂—and six ternary eutectics occur in it. Figs. 5(A) and 5(B) show the general form of the liquidus surface and the phase distribution of the ternary system. There is again considerable solid-solution formation. Along the metasilicate join an unbroken monoclinic series of solutions is formed between clinoenstatite and diopside. Diopside is also partially soluble in CaO.SiO₂—to the extent of 17% in the β form and 16% in the α form. Monticellite, which is orthorhombic, occurs on the orthosilicate join, and can dissolve about 10% of forsterite (a minimum figure). It does not itself apparently dissolve appreciably in either forsterite or 2CaO.SiO₂. The mineral merwinite (3CaO.MgO.2SiO₂) lies on this join between 2CaO.SiO₂ and monticellite, but does not appear in Fig. 5(A), as Ferguson and Merwin, on whose work the diagram is based, did not find it in their synthetic melts.* (It lies in a composition range difficult to study because of the high melting points involved.) It was not till some time later that its occurrence in nature became known. It was then concluded from the manner of its occurrence that it was probably a low-temperature product (forming below the α - β wollastonite inversion temperature), and that it would not normally be expected to form from dry melts. Since then it has been reported in slags,⁽²⁹⁾ but Seil and his collaborators⁽³⁰⁾ failed to find it in pure mixtures of CaO, MgO and SiO₂ of merwinite composition which had been fired to temperatures ranging from 1460° to 1660° C. These observations are not necessarily contradictory, as in complex slags of suitable composition merwinite may be capable of separating directly from a low-melting liquid phase, just as 3CaO.SiO₂ may have fields of direct crystallisation in complex systems containing CaO and SiO₂ (see later). The additional phase boundaries necessitated by its occurrence are indicated by broken lines in Fig. 5(B). As shown in Fig. 5(A), solid-solution formation by CaO.SiO₂ is not confined to the direction of the metasilicate join.

* See Addendum, p. 695 P.

The α solid solutions cover a roughly triangular area bounded by the metasilicate join and the $\text{CaO} \cdot \text{SiO}_2$ -akermanite join, the saturation limit in the latter direction corresponding to 25% of akermanite. The β solid solutions are even more extensive and are capable of holding in solution up to 65% of akermanite. They also include the

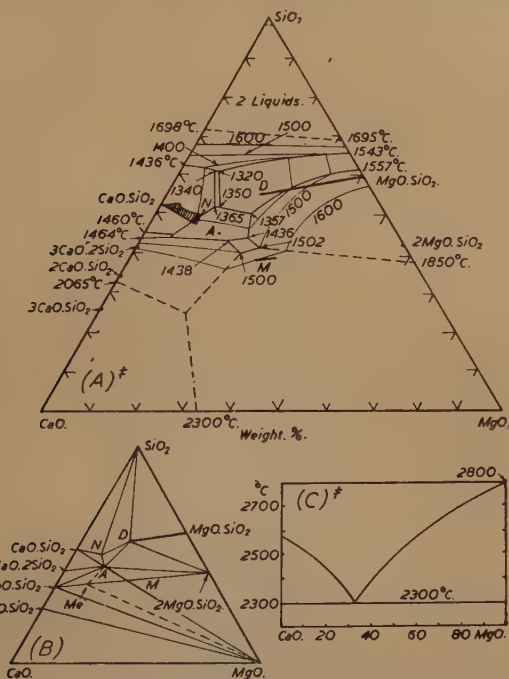


Fig. 5.*—System CaO-MgO-SiO_2 #. (A) Liquidus surface (Ferguson and Merwin,⁽¹¹⁾ Greig,⁽¹⁰⁾ Hall and Insley⁽²⁸⁾). (B) Phase distribution. A = akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), D = diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), M = monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$), Me = merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), N = $5\text{CaO} \cdot 2\text{MgO} \cdot 6\text{SiO}_2$. (C) Thermal equilibrium diagram of the system CaO-MgO (Rankin and Merwin⁽³¹⁾).

composition corresponding to the compound $5\text{CaO} \cdot 2\text{MgO} \cdot 6\text{SiO}_2$. Only a limited range of these β solutions is stable up to the temperature of liquid formation, however.† Fig. 5(C) is the binary diagram of the system MgO-CaO ,⁽³¹⁾ which is eutectiferous and thus gives rise in the ternary diagram to a binary eutectic trough, which runs to a ternary eutectic of uncertain location.

* See Addendum, p. 695 P.

† In the recent paper by Osborn and Schairer⁽¹⁷⁹⁾ it is stated that Schairer and Bowen, in an as yet unpublished research, have reinvestigated the system wollastonite-akermanite and have found no appreciable solid solubility of akermanite in either α - or β -wollastonite.

There have been no systematic investigations of the systems CaO-MnO-SiO_2 and MgO-MnO-SiO_2 . The metasilicate join of the former has, however, been studied, and Fig. 6(A) is the thermal equilibrium diagram of the system $\text{CaO.SiO}_2\text{-MnO.SiO}_2$ according to Voos.⁽³²⁾ It is based on a study of synthetic melts, and shows an unbroken series of solid solutions between wollastonite and rhodonite. This conclusion does not agree very well with the results of studies of the natural manganiferous pyroxenes (with the exception of that by Hey,⁽³³⁾ whose findings in this respect appear to be erroneous). Thus, according to Wyckoff, Merwin and Washington,⁽³⁴⁾ the triclinic mineral bustamite, which is to be regarded as a member of this series approximating to the composition $\text{CaMnSi}_2\text{O}_6$, is structurally similar to triclinic wollastonite (this was also deduced by Bowen, Schairer and Posnjak⁽¹²⁾) but different from rhodonite.

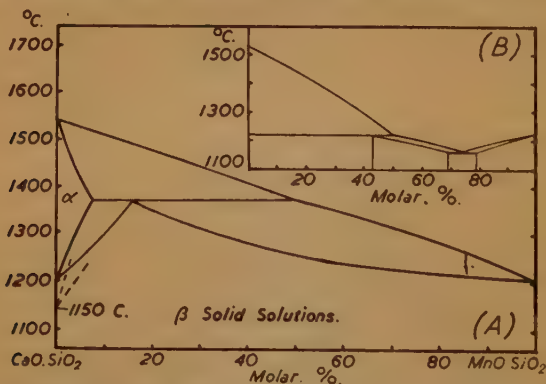


FIG. 6.—(A) Thermal Equilibrium Diagram of the System $\text{CaO.SiO}_2\text{-MnO.SiO}_2$ according to Voos.⁽³²⁾ Broken lines show modification necessitated by redetermination of α - β inversion temperature by Bowen, Schairer and Posnjak⁽¹²⁾ (see also first footnote to Section IV.(c)). (B) Diagram proposed by Sundius.⁽³⁵⁾

Sundius⁽³⁵⁾ arrived at similar conclusions from optical studies of these minerals and published, prior to Voos, a diagram (Fig. 6(B)) which shows an immiscibility gap between bustamite and rhodonite covering the range from 21 to 33% (molar) of CaO.SiO_2 , with the formation of a eutectic between the two saturated solid solutions. A range of apparent insolubility is also shown in the wollastonite series extending from wollastonite to approximately 45 molar-% of MnO.SiO_2 . This was attributed by Sundius to the fact that melts in this range freeze to give pseudo-wollastonite, which does not form solid solutions with MnO.SiO_2 . If this is correct, some revision of his diagram will be necessary, as it was published prior to Bowen, Schairer and Posnjak's redetermination of the wollastonite inversion temperature at 1150° C.,⁽¹²⁾ and indicates an inversion temperature of about 1210° C. apparently. Another

complication, not indicated on the diagram, arises from the fact that bustamite is known to transform on cooling to monoclinic johannsenite ($\text{CaMnSi}_2\text{O}_6$), the relationship between the two being the same as that between iron-containing wollastonite and hedenbergite (Fig. 3(D)). Bowen, Schairer and Posnjak⁽¹²⁾ place the bustamite-johannsenite inversion temperature at 830°C .

According to Greer⁽³⁶⁾ there is complete solid solubility between $2\text{CaO} \cdot \text{SiO}_2$ and tephroite, but this is apparently regarded as doubtful by Bowen, Schairer and Posnjak,⁽¹²⁾ particularly as regards the composition range from 50 to 70% of $2\text{CaO} \cdot \text{SiO}_2$. The orthorhombic mineral glaucochroite ($\text{CaO} \cdot \text{MnO} \cdot \text{SiO}_2$) is, however, known to occur.*

(d) *SiO_2 /Basic-Oxide Systems Higher than Ternary.*

Though there are few data beyond isolated observations, it is to be expected that a feature of such systems will be the occurrence of orthosilicate and metasilicate solid-solution series in which the basic oxides (FeO , MnO , CaO and MgO) will be mutually replaceable by one another, so that "mixed" orthosilicates and metasilicates containing up to four basic oxides will be formed. Neither series will, however, be continuous and unbroken over its entire possible composition range, owing to the gaps existing in certain of the "binary" solution series described above. In addition, complications will be introduced by the polymorphism of $2\text{CaO} \cdot \text{SiO}_2$ in the case of the orthosilicates, and of $\text{CaO} \cdot \text{SiO}_2$ and $\text{MgO} \cdot \text{SiO}_2$ in that of the metasilicates. With regard to the first-mentioned series, observations on the natural olivines suggest that fayalite, tephroite and forsterite are probably miscible in all proportions. The minerals knebelite ($\text{FeO} \cdot \text{MnO} \cdot \text{SiO}_2$), picrotephroite ($\text{MgO} \cdot \text{MnO} \cdot \text{SiO}_2$) and chrysolite ($\text{MgO} \cdot \text{FeO} \cdot \text{SiO}_2$) are essentially "binary" combinations of these three silicates. $2\text{CaO} \cdot \text{SiO}_2$, on the other hand, can be only partially soluble in the solid solutions formed by the other three, as there is immiscibility between it and monticellite, lime-iron olivine and (probably) glaucochroite, respectively. There is also, according to Ferguson and Merwin,⁽¹¹⁾ a gap between monticellite and forsterite. Between monticellite, lime-iron olivine and glaucochroite themselves, however, there is, or so mineralogists believe, complete miscibility. Another significant fact, commented on by Bowen, Schairer and Posnjak,⁽¹⁷⁾ and arising probably from phase-composition relationships in this series, is that natural magnesium-iron olivines are invariably very low in CaO , usually containing less than 2% of this oxide. Fig. 7(A) shows a tentative attempt to depict qualitatively the homogeneity limits of the "quaternary" orthosilicate series consistent with these observations. It has been assumed that MnO as well as FeO will cause a closing of the gap between the monticellites and the olivines proper. This agrees in part with Greer's conclusions⁽³⁶⁾ and is consistent with the

* See also Addendum, p. 695 P, with regard to manganese merwinite.

fact that the manganese ion is nearer in size to the calcium ion than is that of iron, so that replacement of manganese by calcium is likely to be at least as extensive as replacement of iron by calcium. Similarly, the more restricted replaceability of magnesium by cal-

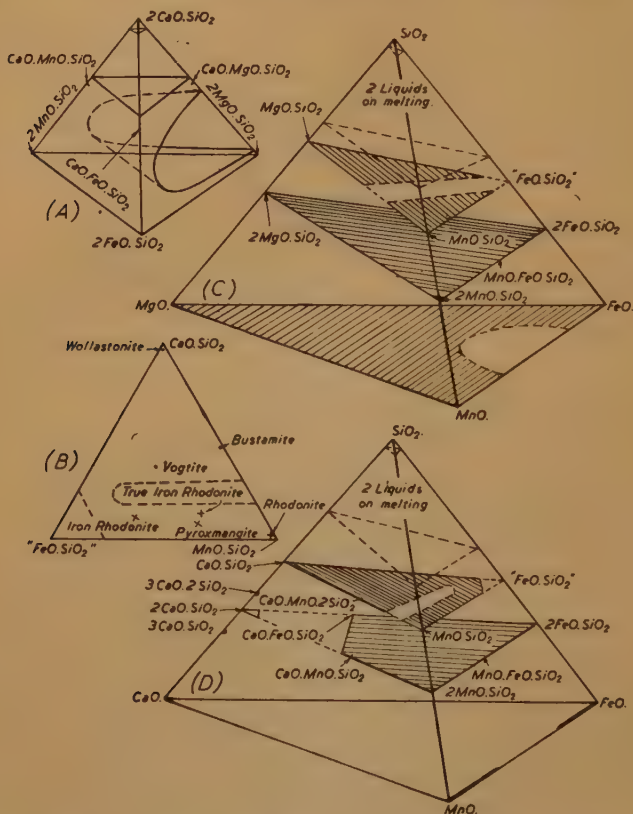


FIG. 7.*—Quaternary Basic-Oxide/Silica Systems. (A) Homogeneity limits of orthosilicate solid-solution series (tentative). (B) Triclinic meta-silicate series showing approximate position of suggested immiscibility gap. Dots denote wollastonites, \times pyroxmangite structure, and $+$ true rhodonite structure. (C) Phases of system $\text{MgO}-\text{MnO}-\text{FeO}-\text{SiO}_2$. (D) Phases of system $\text{CaO}-\text{MnO}-\text{FeO}-\text{SiO}_2$.

cium is consistent with the larger difference between the sizes of these two ions. This may account for the gap between monticellite and forsterite, though they are structurally similar. In this connection it has been pointed out⁽¹⁷⁾ that all the magnesium ions in forsterite are not structurally equivalent, there being two kinds in equal

* See Addendum, p. 695 P.

numbers. The compound monticellite results when all of one kind of atom is replaced by calcium. Apparently most of the intermediate composition range is unstable, possibly because it requires the degree of "order" present in the monticellite replacement to confer stability on the structure.

In the case of the metasilicates, at least three different solid-solution series, orthorhombic, monoclinic and triclinic, are possible, and relationships between them in silicate systems higher than ternary must be of considerable complexity. The orthorhombic series is represented by the enstatite—"FeO.SiO₂" solid solutions, which include the mineral hypersthene (MgO.FeO.2SiO₂). Orthorhombic solid solutions will also be formed over part of the composition range at least (and at suitable temperatures) in all series of which MgO.SiO₂ is an end-member. The monoclinic series includes the clino-enstatite—"FeO.SiO₂" and the clino-enstatite-diopside series, the hedenbergite series and johannsenite. It is likely that clino-enstatite, diopside, hedenbergite and "FeO.SiO₂" form a continuous series (falling short, possibly, of the composition "FeO.SiO₂"). The natural augities and pigeonites are essentially members of this series, and at least one slag mineral (composition : 82 "FeO.SiO₂", 8CaO.SiO₂, 10MgO.SiO₂) belonging to it has been reported.⁽³⁷⁾ At the same time it is quite likely that johannsenite will form continuous series with hedenbergite and diopside. Evidence of its solubility with the former of these two minerals is provided by the manganhedenbergites, described as isomorphous mixtures of johannsenite and hedenbergite. The triclinic series appears to be the one most commonly represented in slags. For example, the "iron rhodonites" of Whiteley and Hallimond⁽²³⁾ belonged to this system. In addition, those authors found that when the CaO content of their slags was more than about 8% a new metasilicate, containing about 15% of CaO, appeared. This new constituent, which they described as an anorthic metasilicate of CaO, MnO and FeO (plus some MgO), has been identified with vogtite, a mineral previously described in slags by Hlawatsch,* and since shown to be isomorphous with wollastonite and bustamite.^(17, 18, 37) The appearance of vogtite in this way suggests the existence of a gap separating, wholly or partly, the wollastonite-bustamite-vogtite series from that of which the "iron rhodonites" and pyroxmangite are members. As already indicated, Sundius⁽³⁵⁾ has previously suggested that such a gap may exist in the "binary" wollastonite-rhodonite series between bustamite and rhodonite. The position of this gap in the composition triangle CaO.SiO₂-MnO.SiO₂-"FeO.SiO₂" is shown tentatively in Fig. 7(B). According to Sundius' observations still another series, corresponding to natural rhodonite and true iron rhodonite, exists but its relationship to the other two series is uncertain.

In spite of the lack of data it is of interest, and not without

* See Bowen, Schairer and Posnjak.⁽¹⁷⁾

value—since it brings us a stage nearer to understanding the constitution of complex furnace slags—to construct tentative phase diagrams of the quaternary silicate systems. This has been done in the light of the evidence reviewed above for the systems MnO-MgO-FeO-SiO_2 and CaO-MnO-FeO-SiO_2 , as shown in Figs. 7(C) and 7(D). Both diagrams purport to hold for a temperature of approximately 960°C. , at which 2CaO.SiO_2 will be in the β form, and " FeO.SiO_2 " will form triclinic wollastonites with CaO.SiO_2 and orthorhombic pyroxenes with MgO.SiO_2 . In the former, complete miscibility of the orthosilicates is assumed, but a gap is shown in the metasilicate series separating the fields of the orthorhombic and the triclinic pyroxenes. This gap must presumably lie close to the MnO.SiO_2 -" FeO.SiO_2 " join, as Sundius has described an orthorhombic pyroxene containing 84.5% of $(\text{FeMn})\text{O.SiO}_2$, the rest being mainly MgO.SiO_2 . The metasilicate series shown in Fig. 7(D) is the triclinic one depicted in Fig. 7(B).

(e) *Systems of Al_2O_3 with Basic Oxides.*

Al_2O_3 combines with FeO , MnO and MgO to form the spinels $\text{FeO.Al}_2\text{O}_3$ (hercynite), $\text{MnO.Al}_2\text{O}_3$ (mangano-spinel) and $\text{MgO.Al}_2\text{O}_3$ (spinel). These are cubic minerals of similar crystal structure, and exhibit extensive solid solubility in one another and in other members of the spinel group of minerals, which includes Fe_3O_4 , $\text{MnO.Fe}_2\text{O}_3$ (jacobsonite) and $\text{FeO.Cr}_2\text{O}_3$ (chromite). Another characteristic property of the spinels is their tendency to form extensive solid solutions with excess Al_2O_3 and Fe_2O_3 . This is now attributed to the fact that these two oxides, which as normally prepared have the corundum (rhombohedral) or α structure, can also exist in so-called γ forms. These have essentially the spinel structure but with a deficiency of metal ions, since the normal spinel structure contains 3 metal ions to every 4 of oxygen. According to McIntosh, Rait and Hay,⁽³⁸⁾ to whom Fig. 8(A) is due, $\text{FeO.Al}_2\text{O}_3$ shows no appreciable solubility of this type, but the compound $3\text{FeO.Al}_2\text{O}_3$ is postulated as forming below the temperature of liquid formation. The reduction curves of Schenck, Franz and Willeke⁽³⁹⁾ give no indication of the occurrence of this compound at 800° or 900°C. , but, on the other hand, they suggest that the join $\text{FeO-FeO.Al}_2\text{O}_3$ may not be a true binary one, as $\text{FeO.Al}_2\text{O}_3$ containing a certain proportion of Fe_3O_4 in solid solution may be stable in contact with metallic iron, as shown in Fig. 20(D). Incidentally, as a consequence of the relationships suggested in the latter figure, a certain degree of reaction between separating solid and residual liquid during freezing would be expected, which might explain the occurrence of an apparently altered zone in some of the $\text{FeO.Al}_2\text{O}_3$ crystals in the melts of McIntosh, Rait and Hay. In both $\text{MnO.Al}_2\text{O}_3$ and $\text{MgO.Al}_2\text{O}_3$ a considerable variation in the ratio of the basic oxide to Al_2O_3 is possible, as shown in Figs. 8(B)⁽¹⁹⁾ and 8(C).^(40, 31, 41)

Structurally, the spinels are to be regarded as mixed oxides;

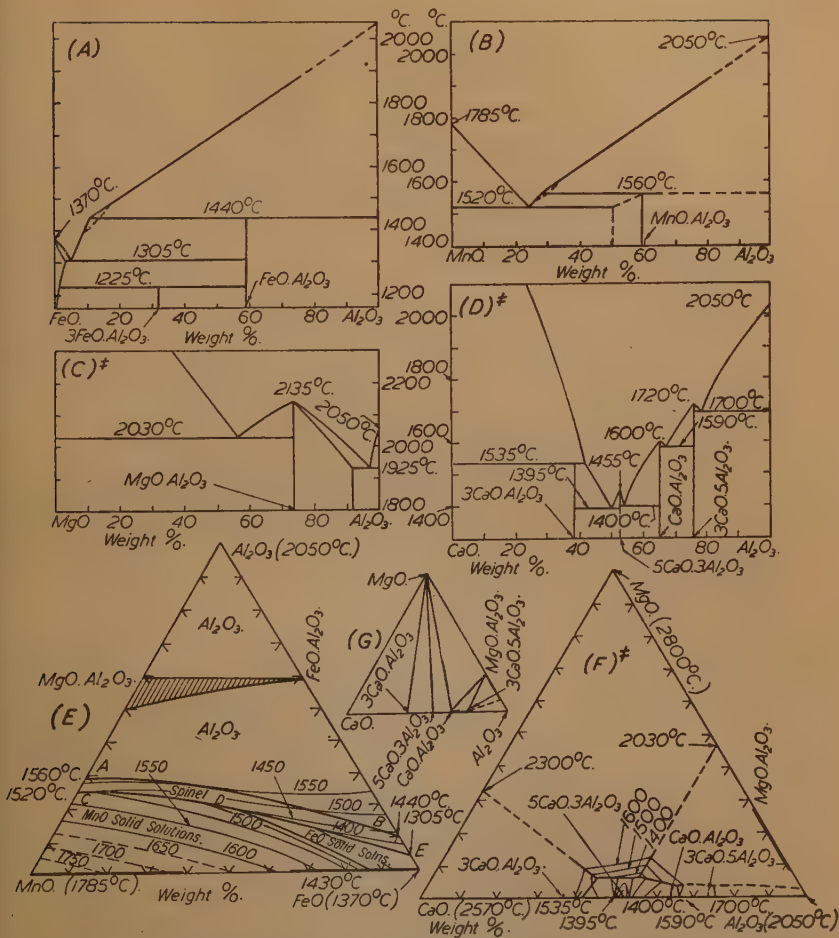


FIG. 8.—Thermal Equilibrium Diagrams of Basic-Oxide/Alumina Systems. (A) System FeO-Al₂O₃ * (McIntosh, Rait and Hay⁽³⁸⁾). (B) System MnO-Al₂O₃ * (Hay, White and McIntosh⁽¹⁸⁾). (C) System MgO-Al₂O₃ # (Rankin and Merwin,^(31, 41) Shepherd, Rankin and Wright⁽⁴⁰⁾). (D) System CaO-Al₂O₃ # (Day, Shepherd and Wright,⁽⁸⁾ Rankin and Wright⁽⁹⁾). (E) Liquidus surface of system FeO-MnO-Al₂O₃ with primary phases in equilibrium with liquid indicated (Hay, McIntosh, Rait and White⁽⁴²⁾). (F) Liquidus surface of system CaO-MgO-Al₂O₃ # (Rankin and Merwin⁽³¹⁾). (G) Phase distribution of the system CaO-MgO-Al₂O₃ (Rankin and Merwin⁽³¹⁾).

* Corrections to the liquidus curves indicated by broken lines necessitated on theoretical grounds.

the calcium aluminates, on the other hand, have the structure of true oxygen salts. The difference from the point of view of the reactions that occur during slag formation in the furnace is possibly small, but it is of significance from the viewpoint of the constitution of the solid slag, since, as a consequence, there is little, if any, solid solubility between the spinels and the calcium aluminates. The system $\text{CaO-Al}_2\text{O}_3$ is shown in Fig. 8(D);^(8, 9) it differs from the spinel systems in the number of compounds occurring and in the relatively very pronounced fluxing action which the two highly refractory components have on each other.

Only two of the ternary systems of the basic oxides and Al_2O_3 appear to have been studied. The ternary system $\text{FeO-MnO-Al}_2\text{O}_3$,⁽⁴²⁾ the liquidus of which is shown in Fig. 8(E), is of a very simple type, as there is complete solubility between $\text{FeO}.\text{Al}_2\text{O}_3$ and $\text{MnO}.\text{Al}_2\text{O}_3$. In the figure, *AB* is the intersection of the plane of peritectic dissociation of the spinel solid-solution series with the liquidus surface, while *CDE* is a eutectic trough joining the eutectics of the $\text{FeO-Al}_2\text{O}_3$ and $\text{MnO}.\text{Al}_2\text{O}_3$ binary systems. For most of its length it is a binary eutectic between spinel solid solutions and FeO-MnO solid solutions. The point *D*, however, is a ternary invariant point necessitated by the gap in the FeO-MnO series. It will be a reaction point, not a ternary eutectic, as *CDE* slopes throughout its length from *C* to *E*.

The ternary system $\text{CaO-MgO-Al}_2\text{O}_3$ ⁽³¹⁾ is more complex, owing to the number of compounds formed between CaO and Al_2O_3 and the absence of solid solubility. Fig. 8(F)# shows the liquidus surface. There are six invariant points, of which two are ternary eutectics, the others being reaction points. No ternary compounds occur.

(f) Fe_2O_3 /Basic-Oxide Systems.

Of these, the system $\text{FeO-Fe}_2\text{O}_3$ is part of the wider system iron-oxygen, which is discussed separately below. Consideration of other systems in which more than one oxide of iron occurs (*i.e.*, involving equilibria between the oxides of iron) is also deferred until after the simpler iron-oxygen system has been described. Fig. 9, however, shows the systems $\text{CaO-Fe}_2\text{O}_3$ ^(43, 44) and $\text{MgO-Fe}_2\text{O}_3$,⁽⁴⁵⁾ the former of which is of particular importance in the study of basic slags. Neither is a true binary system, as dissociation of the Fe_2O_3 occurs at high temperatures, even when heating is carried out in oxygen. In the former system, which was determined at an oxygen pressure of over an atmosphere, this is confined mainly to the range $\text{CaO.Fe}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (*i.e.*, to compositions containing free Fe_2O_3), since $2\text{CaO.Fe}_2\text{O}_3$ and $\text{CaO.Fe}_2\text{O}_3$ are stable in oxygen up to their melting points, and, though some dissociation of these compounds occurs on melting, this is reversible on freezing if the cooling rate is not too rapid. Nevertheless, even in the range $\text{CaO-CaO.Fe}_2\text{O}_3$, measurable dissociation occurs within the melting range, so that the

liquidus curve shown is not that of the pure system, but is rather a curve lying on the liquidus surface of the ternary system $\text{CaO-FeO-Fe}_2\text{O}_3$ (or, more generally, $\text{CaO-Fe-Fe}_2\text{O}_3$). The temperatures indicated will, therefore, be somewhat lower than those of the pure binary system. The melting point indicated in Fig. 9(A) for Fe_2O_3 is actually that of a solid solution of Fe_2O_3 in Fe_3O_4 , since dissociation to the latter oxide occurs during heating. The relationships of Fig. 9(B)[#] were determined in air, *i.e.*, at an oxygen pressure of 15.2 cm. of mercury. Under these conditions the Fe_2O_3 of $\text{MgO.Fe}_2\text{O}_3$ dissociates appreciably even below the melting point (*see* Section VI. (d) below). The solid solutions shown, therefore, contain appreciable FeO at high temperatures. This is particularly the case for compositions to the right of the compound $\text{MgO.Fe}_2\text{O}_3$, which all consist of a single solid-solution phase at high temperatures, this being essentially a solid solution of Fe_3O_4 (formed by the dissociation of Fe_2O_3) in $\text{MgO.Fe}_2\text{O}_3$. The temperatures at which this single phase is formed are indicated by the solubility, or rather transformation, curve on the right of the diagram terminating at 1386°C. , the temperature, according to Roberts and Merwin,⁽⁴⁵⁾ at which pure Fe_2O_3 transforms to Fe_3O_4 in air.* There is thus complete solid solubility between $\text{MgO.Fe}_2\text{O}_3$ and Fe_3O_4 , both of which are spinels. The calcium ferrites are not spinels, and do not form solid solutions with them. The infusibility of the spinels relative

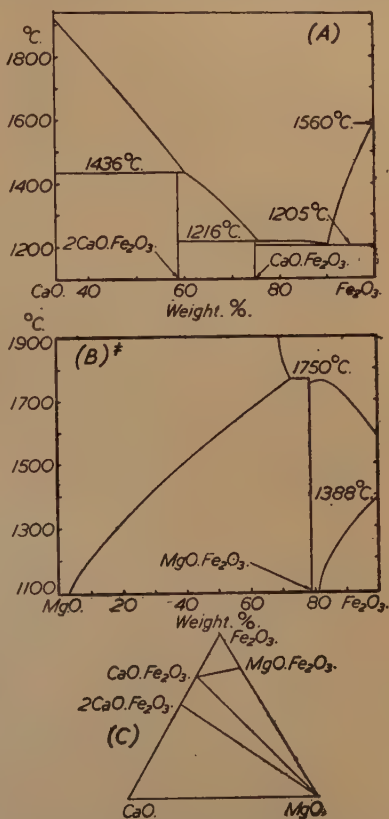


FIG. 9.—Basic-Oxide/ Fe_2O_3 Systems. (A) Thermal equilibrium diagram of the system $\text{CaO-Fe}_2\text{O}_3$ (Sosman and Merwin[#], White, Graham and Hay⁽⁴⁴⁾). (B) Thermal equilibrium diagram of the system $\text{MgO-Fe}_2\text{O}_3$ # (Roberts and Merwin⁽⁴⁵⁾). (C) Phase diagram of the system $\text{CaO-MgO-Fe}_2\text{O}_3$ (Hay and White⁽⁴⁶⁾).†

* This temperature has since been redetermined by Greig, Posnjak, Merwin and Sosman⁽⁸⁶⁾ to be 1388°C. , and this figure has been inserted in Fig. 9(B).

† See Addendum, p. 695 P.

to the corresponding calcium compounds is again brought out by comparison of Figs. 9(A) and 9(B).

Little is known of the system $\text{MnO-Fe}_2\text{O}_3$ beyond that it contains the spinel $\text{MnO.Fe}_2\text{O}_3$, which occurs naturally as jacobsite (see Fig. 20(A)).

The phase distribution in the system $\text{CaO-MgO-Fe}_2\text{O}_3$ * (which becomes quaternary in the field $\text{CaO.Fe}_2\text{O}_3\text{-MgO.Fe}_2\text{O}_3\text{-Fe}_2\text{O}_3$ owing to dissociation of the free Fe_2O_3) has been given by Hay and White⁽⁴⁶⁾ as shown in Fig. 9(C). They regard the join $\text{MgO-2CaO.Fe}_2\text{O}_3$ as definitely established, and, in fact, there is ample confirmation of it from observations on cement and dolomite clinkers. The join from MgO to $\text{CaO.Fe}_2\text{O}_3$ they regard as probably, but not definitely, established by their work, which was of an exploratory nature, being based on "pill" fusibility tests combined with microscopic examination of the resultant melts. This would indicate that both $2\text{CaO.Fe}_2\text{O}_3$ and $\text{CaO.Fe}_2\text{O}_3$ form preferentially to (i.e., have greater stability than) $\text{MgO.Fe}_2\text{O}_3$ in $\text{CaO-MgO-Fe}_2\text{O}_3$ mixtures. (See, however, discussion of Fig. 20(F), Section VI.(f).) The most fusible compositions were found to lie in the field $\text{CaO.Fe}_2\text{O}_3\text{-MgO.Fe}_2\text{O}_3\text{-Fe}_2\text{O}_3$ adjacent to the fusible range of the system $\text{CaO-Fe}_2\text{O}_3$. There was some evidence of a trough running from this low-melting region towards the CaO-MgO eutectic.

(g) $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{Basic-Oxide Systems}$.

The radii of trivalent Al and Fe ions in 6-fold co-ordination are 0.57 Å. and 0.67 Å., respectively, which gives rise to the expectation that a certain degree of mutual replaceability should occur in their compounds. Hence solid-solution formation should be a feature of systems in which both Al_2O_3 and Fe_2O_3 occur. The binary system $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ has not been completely investigated, but it is known that there is considerable solid solubility, at least of Al_2O_3 in Fe_2O_3 . Thus, Hansen and Brownmiller⁽⁴⁷⁾ found approximately 14% solubility of Al_2O_3 in Fe_2O_3 in mixtures of the precipitated oxides heated to 1200° C. This agrees reasonably well with the figure of 12% obtained earlier by Forestier and Chaudron.⁽⁴⁸⁾ The former authors also found evidence of some solubility of Fe_2O_3 in Al_2O_3 as shown by the slight shift of the lines in the X-ray spectrum of Al_2O_3 that occurred in the presence of Fe_2O_3 . Because of the temperature employed, these figures will apply to the α or rhombohedral forms of the oxides. So far as the author is aware, no figures for the solubilities of the γ or spinel forms have been published.†

The lime-rich regions of the system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ were studied by Hansen, Brownmiller and Bogue,⁽⁴⁹⁾ who found partial solid solubility between $\text{CaO.Al}_2\text{O}_3$ and $\text{CaO.Fe}_2\text{O}_3$, and complete

* See Addendum, p. 695 P.

† According to Gmelins, "Handbuch der anorganischen Chemie," "Eisen," B-5, p. 1113, Passerini⁽¹⁹⁴⁾ claims to have found 25% solubility of Al_2O_3 in Fe_2O_3 , and 19.6% solubility of Fe_2O_3 in Al_2O_3 in mixtures heated to only 600° C., at which temperature Al_2O_3 at least would not be converted to the α form.

solid solubility between $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and a ternary compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (brownmillerite), this latter series representing the effect of progressive replacement of half of the Fe_2O_3 of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ by Al_2O_3 . Phase relations within this system, and the principal melting temperatures are shown in Figs. 10(A), 10(B) and 10(C). The systems formed by Fe_2O_3 and Al_2O_3 with the spinel-forming basic oxides have not yet been studied to any great extent. Study of the spinels formed by natural and industrial processes, however, indicates that fairly extensive replaceability of Fe_2O_3 by

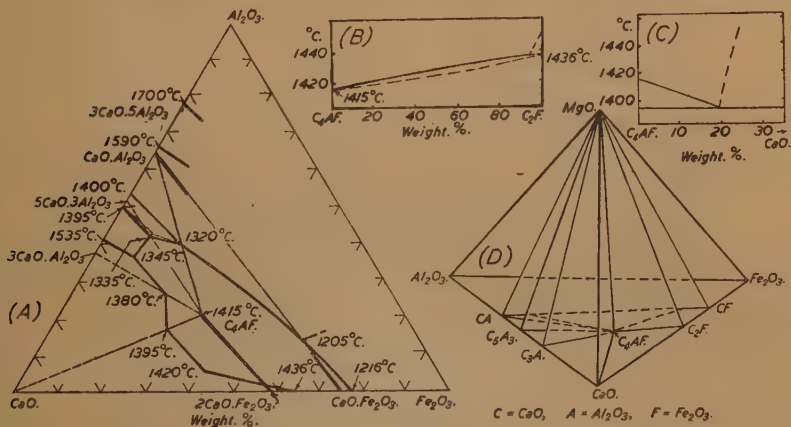


FIG. 10.— $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{Basic-Oxide}$ Systems. (A) Liquidus surface and phase distribution in lime-rich portion of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ (Hansen, Brownmiller and Bogue⁽⁴⁹⁾). (B) Thermal equilibrium diagram of the system $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 - 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (Hansen, Brownmiller and Bogue⁽⁴⁹⁾). (C) Thermal equilibrium diagram of the system $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 - \text{CaO}$ (Hansen, Brownmiller and Bogue⁽⁴⁹⁾). (D) Probable phase distribution in lime-rich region of the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$.

(C = CaO; F = Fe_2O_3 ; A = Al_2O_3 .)

Al_2O_3 and *vice versa* is the rule in this group of minerals. Hansen and Brownmiller⁽⁴⁷⁾ found that $\text{MgO} \cdot \text{Al}_2\text{O}_3$ could dissolve 9% of $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ while still maintaining its single-phase character.

The last-mentioned workers also studied part of the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ and reported considerable solubility of MgO in the $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 - 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ solid solutions. This is not generally accepted, however, and is, in fact, contradicted by much later work on the constitution of cement and dolomite clinkers. Fig. 10(D) shows the probable phase distribution in the high-lime region of this system.

(h) $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Basic-Oxide}$ Systems.

The relationships between Al_2O_3 and SiO_2 alone are shown in Fig. 11(A).^(50, 51) One compound, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite), occurs

at high temperatures, and forms a eutectic with SiO_2 at $1545^\circ \text{C}.$ * It has recently been found to be capable of existing in different modifications.^(52, 53) Fig. 11(B) indicates the liquidus surface and

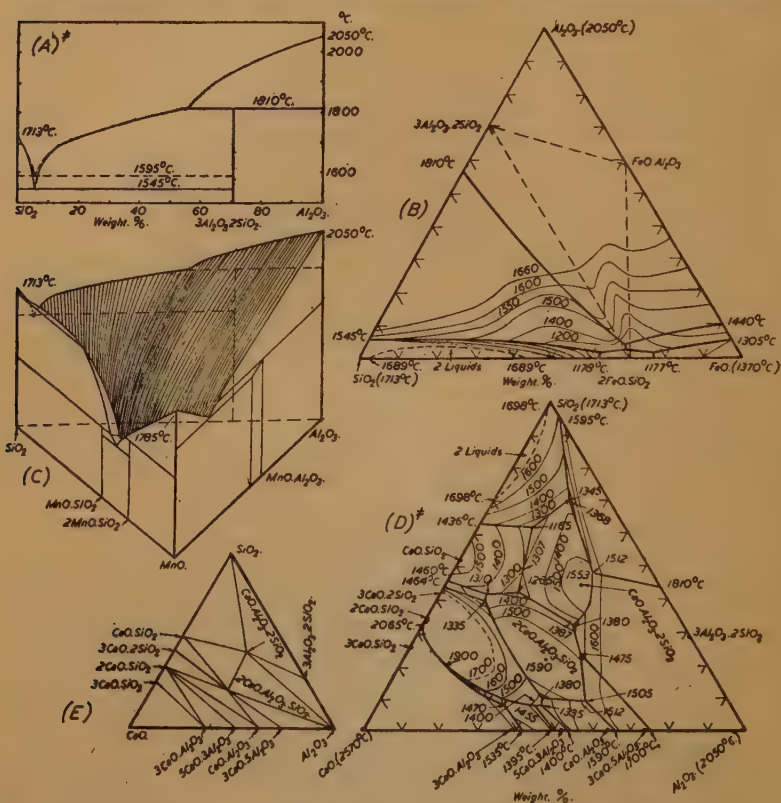


Fig. 11, (A) to (E).— Al_2O_3 - SiO_2 -Basic-Oxide Systems. (A) Thermal equilibrium diagram of the system Al_2O_3 - SiO_2 # (dotted lines on basis of redetermination of eutectic temperature by Schairer and Bowen (see first footnote to Section IV. (h)) (Bowen and Greig,⁽⁵⁰⁾ Greig⁽⁵¹⁾). (B) Liquidus surface and phase distribution of the system FeO - Al_2O_3 - SiO_2 (Hay, White and Caulfield,⁽⁵⁴⁾ Greig⁽⁵⁾). (C) Liquidus surface of the system MnO - Al_2O_3 - SiO_2 (Hay⁽⁵⁵⁾).† (D) Liquidus surface of the system CaO - Al_2O_3 - SiO_2 # (Rankin and Wright,⁽⁹⁾ Bowen and Greig,⁽⁵⁰⁾ Greig⁽¹⁰⁾). According to Schairer,⁽¹⁸⁰⁾ Wright has recently revised the temperatures in this system (unpublished). Temperatures quoted here are those given by Schairer on the basis of this redetermination. (E) Phase distribution in the system CaO - Al_2O_3 - SiO_2 .

* Schairer⁽¹⁸⁰⁾ states that Schairer and Bowen have now established the eutectic temperature as $1595 \pm 10^\circ \text{C}$. An account of their work is at present being prepared for publication.

† See Addendum, p. 695 P.

the phase relationships of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$.⁽⁵⁴⁾ Of the four quintuple points, one is formed by the intersection of the peritectic planes of $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and $\text{FeO}\cdot\text{Al}_2\text{O}_3$ at the liquidus surface, the other three being ternary eutectics. These latter lie in a deep trough which joins the eutectics of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{FeO-Al}_2\text{O}_3$ binary systems, and which, therefore, lies very close to the FeO-SiO_2 side of the diagram. One consequence of this is that the liquid immiscibility present in FeO-SiO_2 melts of high SiO_2 content must disappear when a few per cent. of Al_2O_3 are present. According to Greig⁽⁵⁾ the amount required to cause this is less than 3% (see Fig. 18(G)). The approximate boundary of the zone of immiscibility is indicated in the diagram. The liquidus surface between this boundary and the eutectic trough must be very steep.* Fig. 11(C) shows the liquidus surface of the system $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ as given by Hay in the discussion on a paper by Whiteley.⁽⁵⁵⁾ Details of the phase distribution are not yet available, but the form of the liquidus surface is very similar to that of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$. In neither of these systems have ternary compounds been found in the synthetic melts, though the garnet species

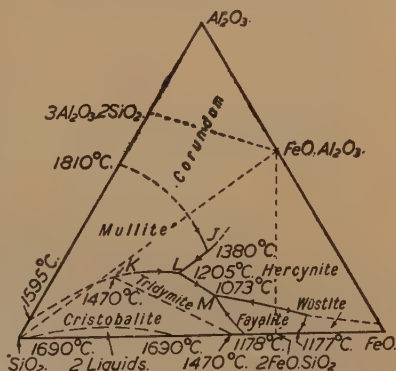


FIG. 11(F).—Liquidus Surface and Phase Distribution of the System $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ according to Schairer # (see footnotes to Section IV.(h)).

* Recently Snow and McGaughey⁽¹⁸¹⁾ and Schairer⁽¹⁸⁰⁾ have published diagrams for the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$, the latter as part of a study of the quaternary system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$. Both are based on the examination of melts quenched after being brought to equilibrium at various temperatures, this being probably the most accurate method available for the determination of equilibria in silicate melts. The two diagrams agree well as regards the location of the invariant points and the phase assemblages associated with them, though the temperatures given by the former workers are about 100°C . lower than Schairer's. This the latter attributes to the presence of impurities in Snow and McGaughey's melts and particularly to the difficulty of measuring the temperature accurately in the large melts employed. Following the usual practice adopted by the Geophysical Laboratory workers, Schairer determined the ferrous- and ferric-oxide contents of all his melts, and for the purpose of plotting on a ternary diagram calculated the total iron content to FeO . His diagram, which must be considered the most accurate yet available, is reproduced in Fig. 11(F). It differs from Fig. 11(B) in that (1) the low-melting trough, particularly towards its high-silica end, is shown to occur at somewhat higher Al_2O_3 contents, (2) the minimum melting temperature is about 100°C . higher (it is difficult to account for this unless it arises from differences in the Fe_2O_3 contents of melts heated in iron and in molybdenum crucibles, respectively), and (3) as regards the phase distribution in the solid system, the tie line $\text{SiO}_2\text{-hercynite}$ will occur instead of the tie line mullite-fayalite . Mullite is, therefore, incapable of co-existing with fayalite.

almandite ($3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and spessartite ($3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) belong essentially to these systems. Similarly, grossularite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) is not found in $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ melts. In nature garnets are usually found in rocks which have been subjected to stress, but the conditions necessary for their formation are not yet fully understood. In the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$,^(9, 50, 10) as determined by the study of synthetic melts, two ternary compounds occur in addition to the various binary compounds, so that the system is somewhat complex. It has become well known to metallurgists because of its application to blast-furnace slags. The part of the diagram directly applicable to open-hearth slags is the region of low Al_2O_3 contents. Fig. 11(D) gives the liquidus surface and indicates the composition of the ternary compounds anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). The phase distribution is shown in Fig. 11(E). A significant feature of this system is the occurrence of a field of primary crystallisation of the compound $3\text{CaO} \cdot \text{SiO}_2$, which is incapable of existing in the presence of the liquid phase in the binary system $\text{CaO}-\text{SiO}_2$ (Fig. 1(C)). The field in question occurs as a narrow wedge adjacent to the primary field of CaO ; the upper tip of the wedge, which corresponds to the upper temperature limit of crystallisation, occurs at 1900°C ., the upper limit of stability of $3\text{CaO} \cdot \text{SiO}_2$ in the binary system. The particular significance attached to the occurrence of this field is that similar crystallisation fields of $3\text{CaO} \cdot \text{SiO}_2$ should, in general, occur in systems which contain CaO and SiO_2 in the presence of fluxes. Hence, though $3\text{CaO} \cdot \text{SiO}_2$ forms in $\text{CaO}-\text{SiO}_2$ mixtures only after somewhat prolonged annealing in the solid state,⁽⁸⁾ in more complex systems it may occur more readily as a phase crystallising from the liquid state. It has also been shown that $3\text{CaO} \cdot \text{SiO}_2$ becomes unstable on cooling below a certain temperature.^(56, 57) According to Lea and Parker⁽⁵⁷⁾ the temperature at which this occurs is $1250 \pm 25^\circ \text{C}$., and they state that $3\text{CaO} \cdot \text{SiO}_2$ is apparently unique in thus possessing an upper and lower limit of stability. The low-temperature decomposition is naturally a somewhat sluggish reaction and does not prevent the occurrence of $3\text{CaO} \cdot \text{SiO}_2$ at room temperature. Its effects have, however, been noted in stabilised dolomite clinkers in which the CaO was present mainly as $3\text{CaO} \cdot \text{SiO}_2$.⁽⁵⁸⁾ The system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ has also been studied,⁽⁴¹⁾ but the diagram is not reproduced. It contains the ternary compound cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), which is a product of the firing of fireclay-teatite mixtures.

In all of these ternary systems the action of small percentages of Al_2O_3 is to lower the melting points of the binary basic-oxide/ SiO_2 slags. Of particular importance is its drastic effect on the ranges of liquid immiscibility of the binary systems. This was first shown in a series of investigations by Greig,^(4, 5, 10) who found that less than 3% of Al_2O_3 caused the biliquid ranges of the systems $\text{CaO}-\text{SiO}_2$ and $\text{FeO}-\text{SiO}_2$ (see Figs. 11(B) and 11(D)) to

disappear, while a little less than 5% had the same effect on the MgO-SiO_2 biliquidal range. In each case the addition of Al_2O_3 causes a rapid narrowing of the range, accompanied by a drop in the temperature of immiscible-liquid formation. Further, in each case, outside the closed boundary of the biliquidal zone the liquidus surface slopes steeply downwards to a eutectic trough. Hence, even in small amounts, Al_2O_3 should have a pronounced fluxing effect in acid slags, and should cause a marked increase in the SiO_2 content at

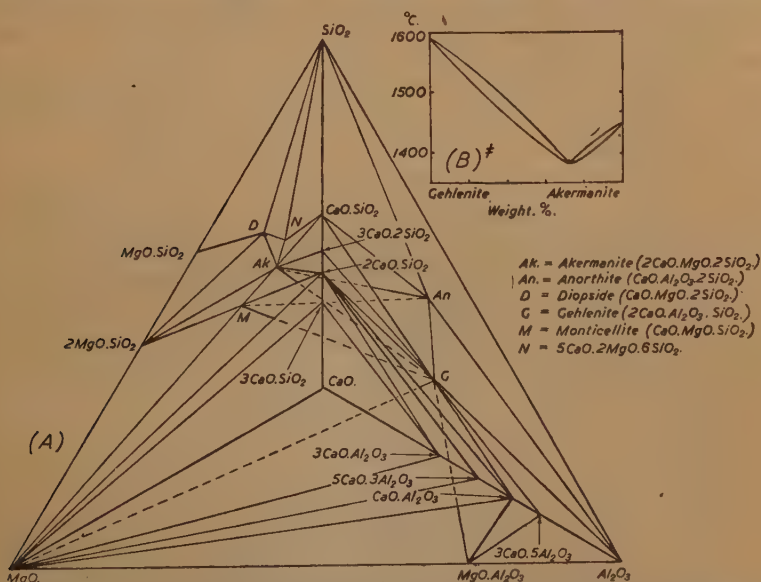


FIG. 12.*—(A) Phase Distribution in the System $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (McCaffery, Oesterle and Schapiro⁽⁶⁰⁾). (B) Thermal Equilibrium Diagram of the System Gehlenite-Akermanite † (Ferguson and Budington⁽⁶¹⁾).

saturation. It will also be obvious that Al_2O_3 must be kept to a minimum in silica bricks, hearths, &c., which are subjected to the attack of basic oxides. Körber's finding⁽⁵⁹⁾ that the presence of 24–27% of Al_2O_3 in a FeO-MnO-SiO_2 slag melted in silica raised the SiO_2 content by a few per cent. only can possibly be attributed to the sluggishness of such a slag, as it is hardly likely, in view of the relationships shown in Figs. 11(B) and 11(C), that saturation with SiO_2 was actually reached.

The quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ * has been the subject of a paper by McCaffery, Oesterle and Schapiro,⁽⁶⁰⁾ who give diagrams to show the phase distribution. One quaternary compound, madisonite, to which the formula $2\text{CaO} \cdot 2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$

* See Addendum, p. 695 P.

was provisionally assigned, was proposed. Phase relations in the high-lime region of the system are shown in Fig. 12(A). In the complete system two binary solid-solution series occur, *viz.*, the metasilicate series between clino-enstatite and diopside described by Bowen⁽¹⁴⁾ and the melilite series formed between akermanite and gehlenite, the thermal equilibrium diagram of which was given by Ferguson and Buddington⁽⁶¹⁾ (Fig. 12(B)). The melting relationships in the partial quaternary system $\text{CaO}-5\text{CaO} \cdot 3\text{Al}_2\text{O}_3-2\text{CaO} \cdot \text{SiO}_2-\text{MgO}$ have been studied by McMurdie and Insley.⁽⁶²⁾ A noteworthy feature is the occurrence of a volume of primary crystallisation of $3\text{CaO} \cdot \text{SiO}_2$.*

The system $\text{FeO}-\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is of particular importance from the point of view of the slagging of casting-pit refractories, but so far no data concerning it have been published.

(i) *The System $\text{Fe}_2\text{O}_3-\text{SiO}_2$.*

This system is incapable of direct study, owing to the impossibility of preventing dissociation of the Fe_2O_3 to Fe_3O_4 or further, this tendency being increased by the presence of SiO_2 . The work of Greig⁽⁵⁾ indicated widespread liquid immiscibility in this system, and Bowen, Schairer and Willems,⁽⁶³⁾ in their work on the system $\text{Na}_2\text{SiO}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$, obtained indications that a eutectic lay close to the composition Fe_2O_3 in the binary system. They concluded that the melting point of Fe_2O_3 was higher than that of SiO_2 , and that the thermal equilibrium diagram would be of the form shown in Fig. 13(A).

(j) *$\text{Fe}_2\text{O}_3/\text{SiO}_2/\text{Basic-Oxide Systems}$.*

There is little information on these systems. Hansen and Bogue⁽⁶⁴⁾ studied the high-CaO region of the system $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ and established the phase distribution shown in Fig. 13(B). At higher contents of Fe_2O_3 and SiO_2 dissociation of the former becomes serious, so that the system must be considered as part of the quaternary system $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. The study of Hay and White⁽⁶⁵⁾ of the fusibility and constitutional relationships in $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ mixtures heated in air falls into this category and is considered later, as is the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$.

(k) *$\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{SiO}_2/\text{Basic-Oxide Systems}$.*

A portion of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ (the system $\text{CaO}-2\text{CaO} \cdot \text{SiO}_2-5\text{CaO} \cdot 3\text{Al}_2\text{O}_3-4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) has been studied by Lea and Parker.⁽⁵⁷⁾ Fig. 13(C) shows the phase distribution, which is relatively simple, since no quaternary compounds occur, there being only three 4-phase quaternary volumes, *viz.*, $\text{CaO}-3\text{CaO} \cdot \text{SiO}_2-4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3-3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2-3\text{CaO} \cdot \text{Al}_2\text{O}_3-2\text{CaO} \cdot \text{SiO}_2-4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3-$

* Reference should also be made to studies by Andersen⁽¹⁸²⁾ and Osborn and Schairer.⁽¹⁷⁹⁾

$2\text{CaO}.\text{SiO}_2-5\text{CaO}.\text{3Al}_2\text{O}_3-4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$. The melting relationships are naturally somewhat more difficult to show, and for a full account of these the original paper by these authors should be consulted. (A very full description of this system is also to be found in the book "The Chemistry of Cement and Concrete" by

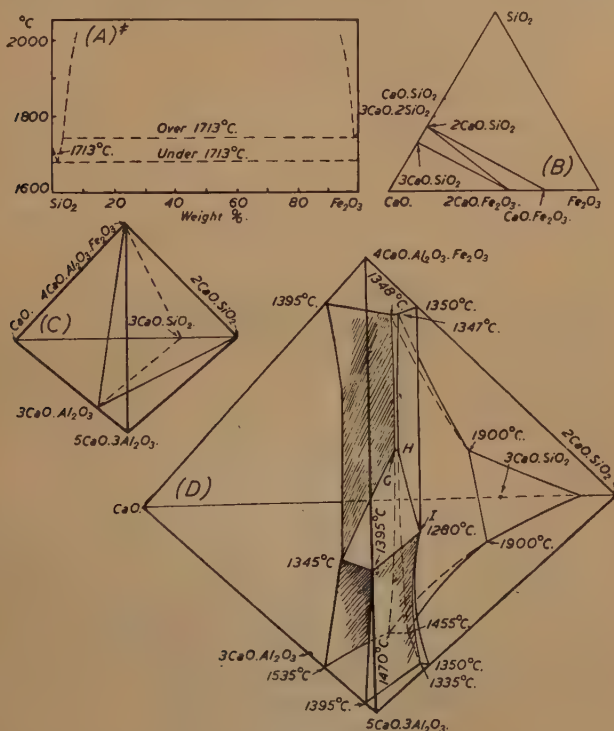


FIG. 13.—(A) Proposed Form of the Thermal Equilibrium Diagram of the System $\text{Fe}_2\text{O}_3-\text{SiO}_2$ # (Bowen, Schairer and Willems⁽⁶³⁾). (B) Phase Distribution in the System $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ (Hansen and Bogue⁽⁶⁴⁾). (C) Phase Distribution in the System $\text{CaO}-2\text{CaO}.\text{SiO}_2-5\text{CaO}.\text{3Al}_2\text{O}_3-4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ (Lea and Parker⁽⁶⁷⁾). (D) Melting Relationships in the System $\text{CaO}-2\text{CaO}.\text{SiO}_2-5\text{CaO}.\text{3Al}_2\text{O}_3-4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ (Lea and Parker⁽⁶⁷⁾). Temperatures of G, H and I are 1341° , 1338° and $1280^\circ \text{C}.$, respectively.

Lea and Desch.⁽⁶⁶⁾ A wedge-shaped field of primary crystallisation of $3\text{CaO}.\text{SiO}_2$ similar to that found in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ occurs in the ternary face $\text{CaO}-5\text{CaO}.\text{3Al}_2\text{O}_3-4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$, corresponding boundaries of these fields being joined by planes passing through the quaternary tetrahedron, the volume thus enclosed being the primary crystallisation volume of $3\text{CaO}.\text{SiO}_2$ in

the quaternary system (see Fig. 13(D)). It appears likely that, in the wider system $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$, this volume will extend to the face $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. In the narrower system three sextuple points, *G*, *H* and *I* of Fig. 13(D), occur, corresponding to equilibrium between (1) CaO , $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, (2) $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and (3) $3\text{CaO} \cdot \text{Al}_2\text{O}_3-2\text{CaO} \cdot \text{SiO}_2$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$

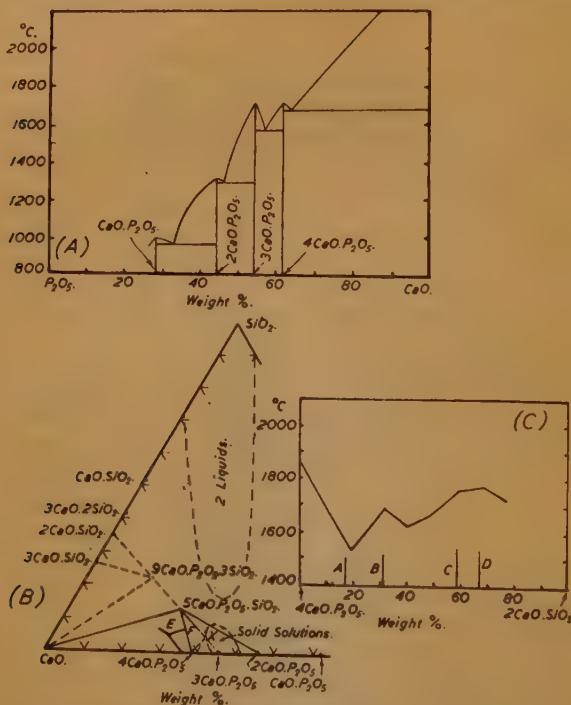


FIG. 14.*—(A) The Thermal Equilibrium Diagram of the System $\text{CaO}-\text{P}_2\text{O}_5$ (Trömel^(67, 68)). (B) Suggested Phase Fields in the System $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ after Körber and Trömel^(69, 70) and Behrendt and Wentrup.⁽⁷¹⁾ (C) Melting-Point Curve of $4\text{CaO} \cdot \text{P}_2\text{O}_5-2\text{CaO} \cdot \text{SiO}_2$ Mixtures (Blome⁽⁷⁸⁾).

and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, the temperatures of these being 1341° , 1338° and 1280°C . *I* is a quaternary eutectic lying extremely close to the ternary plane $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3-2\text{CaO} \cdot \text{SiO}_2-4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The two others are reaction points.

(1) *The Systems $\text{CaO}-\text{P}_2\text{O}_5$ and $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$.**

Fig. 14(A) shows the thermal equilibrium diagram of part of the system $\text{CaO}-\text{P}_2\text{O}_5$ as given by Trömel^(67, 68) and by Körber and

* See Addendum, p. 695 r.

Trömel.^(69, 70) Four compounds occur in the range studied, and of these $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and $2\text{CaO} \cdot \text{P}_2\text{O}_5$ both undergo polymorphic change from α to β forms on cooling, the former at about 1400°C . The CaO -rich region of this system up to approximately 50% of P_2O_5 has also been studied by Behrendt and Wentrup⁽⁷¹⁾ and their diagram over this range agrees substantially with Fig. 11(A), though they give somewhat higher temperatures for the melting points of $4\text{CaO} \cdot \text{P}_2\text{O}_5$ (hilgenstockite) and $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (1750 – 1770° and about 1790°C ., respectively) and for the temperature of the α – β change in the latter compound (1460 – 1480°C .). Earlier workers (Forster,⁽⁷²⁾ Dieckmann and Houdremont⁽⁷³⁾ and others) had described the formation of what was believed to be the compound oxyapatite, $\text{CaO} \cdot 3(3\text{CaO} \cdot \text{P}_2\text{O}_5)$ or $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$, on slow cooling or annealing of $4\text{CaO} \cdot \text{P}_2\text{O}_5$, or on heating suitable proportions of CaO and P_2O_5 or CaO and $3\text{CaO} \cdot \text{P}_2\text{O}_5$. In the former case the separation of free CaO could also be detected, and it appeared, therefore, that oxyapatite should occur as a phase in the system CaO – P_2O_5 . Neither Körber and Trömel nor Behrendt and Wentrup, however, have found any evidence for the occurrence of this compound in the pure system CaO – P_2O_5 , though their investigations involved the use of thermal, microscopic and X-ray methods of study. After annealing the eutectic mixture of $4\text{CaO} \cdot \text{P}_2\text{O}_5$ and $3\text{CaO} \cdot \text{P}_2\text{O}_5$ in ordinary air between 1100° and 1050°C ., however, Körber and Trömel⁽⁷⁰⁾ obtained evidence of a new crystalline constituent with a structure similar to that of apatite, $\text{Ca}_{10}(\text{F}, \text{Cl})_2(\text{PO}_4)_6$. If the annealing was carried out *in vacuo*, CO_2 , oxygen or air that had been dried with P_2O_5 , no new structure appeared. It was concluded, therefore, that for the formation of the apatite-like compound the presence of moisture was necessary, and that the compound formed was hydroxyapatite, $\text{Ca}(\text{OH})_2 \cdot 3(3\text{CaO} \cdot \text{P}_2\text{O}_5)$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Its remarkable stability was demonstrated by the fact that, once formed, it required a temperature of over 1400°C . to decompose it. These findings are, on the whole, confirmed by most of the recent investigations on the subject, *e.g.*, by those of Schleede, Schmidt and Kindt⁽⁷⁴⁾ and of Bredig, Franck and Fuldner.^(75, 76) In their earlier paper the latter workers had supported the view that oxyapatite was formed, but in their second paper on the subject they report their finding that pure oxyapatite cannot exist, though they claim to have obtained a solid solution of oxyapatite in hydroxyapatite containing between 60% and 70% of the former, and with an X-ray spectrum similar to that of apatite and hydroxyapatite. The natural mineral voelkerite, which was previously supposed to be oxyapatite, may possibly be a solid solution of this type.

The formation of hydroxyapatite in basic Bessemer slags which had been quickly cooled in water was observed earlier by Schneiderhöhn.⁽⁷⁷⁾ It tended to occur mainly round fissures and blow-holes in the slag, presumably because they had, during quenching, been filled with superheated steam, which had caused the decomposition

of the $4\text{CaO} \cdot \text{P}_2\text{O}_5$ normally present in the slag. The latter compound appears to be readily affected in this way, even by the moisture in the atmosphere, the practical importance of this behaviour lying in the fact that hydroxyapatite, like other members of the apatite group, gives a low P_2O_5 solubility in the citric-acid test. Thus Körber and Trömel⁽⁷⁰⁾ give the citric-acid solubility of $4\text{CaO} \cdot \text{P}_2\text{O}_5$ cooled *in vacuo* as 98.5% (this figure representing the percentage of the total phosphorus content soluble in the acid under the conditions of the test). After cooling in air, the solubility was 70.5%, while after annealing at 1100°C . in air it dropped to 14.1%. Precipitated hydroxyapatite annealed at 1100°C . and with a grain size of 10^{-4} cm . gave a solubility of 22.4%, while with a grain size of 10^{-6} cm . it was 74.8%, showing that even this compound could give a moderately high solubility figure if in a fine enough state of division. $3\text{CaO} \cdot \text{P}_2\text{O}_5$ gave 96.8% solubility when in the α form and 53.8% when in the β form.

Part of the ternary system $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ has been studied by Körber and Trömel^(69, 70) and by Behrendt and Wentrup,⁽⁷¹⁾ and Fig. 14(B) summarises the principal findings of those authors. Körber and Trömel established the existence of two ternary compounds, $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ (silico-carnotite), which had previously been identified by several workers in basic-furnace slags, and $9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$, both with a melting point above 1750°C . and with citric-acid solubilities of 96.5% and 97.0%, respectively. They also stated that α - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ had a considerable range of solid solubility extending into the ternary diagram, as shown in Fig. 14(B), and they found evidence of the existence of the liquid immiscibility range of the system $\text{CaO}-\text{SiO}_2$ far into the ternary diagram. Behrendt and Wentrup studied actual melting relationships within a more restricted area of the ternary diagram, and concluded that the joins $4\text{CaO} \cdot \text{P}_2\text{O}_5-5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{P}_2\text{O}_5-5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ were true binary (quasi-binary) sections. They estimated by extrapolation that the melting point of $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ was about 1890°C . In the field $\text{CaO}-4\text{CaO} \cdot \text{P}_2\text{O}_5-5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ a ternary eutectic, melting at $1595-1600^\circ \text{C}$., was found (point *E* of Fig. 14(B)). In the field $4\text{CaO} \cdot \text{P}_2\text{O}_5-5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2-3\text{CaO} \cdot \text{P}_2\text{O}_5$ the eutectic temperature was found to vary between 1570° and 1620°C ., being, therefore, higher than that of the binary $4\text{CaO} \cdot \text{P}_2\text{O}_5-3\text{CaO} \cdot \text{P}_2\text{O}_5$ eutectic at 1568°C . From this they concluded that the join $3\text{CaO} \cdot \text{P}_2\text{O}_5-5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ was not quasi-binary, and that $3\text{CaO} \cdot \text{P}_2\text{O}_5$ probably formed a range of solid solution in this region. The solid lines in Fig. 15(B) show the phase fields indicated by the work of the last-mentioned authors.* Tentative phase fields, which, however, seem reasonably consistent with the observations on actual furnace slags

* There is a discrepancy in the fact that Körber and Trömel's tentative solid-solution range crosses the join $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2-2\text{CaO} \cdot \text{P}_2\text{O}_5$. If the latter is binary the solid-solution range must be more restricted than the diagram indicates.

discussed later, are indicated by broken lines.* A measure of support for the phase distribution suggested is got from an investigation carried out by Blome⁽⁷⁸⁾ on the melting points of $4\text{CaO} \cdot \text{P}_2\text{O}_5 - 2\text{CaO} \cdot \text{SiO}_2$ mixtures. His melting-point curve, which purports to give temperatures at which melting was completed, is reproduced in Fig. 14(C), and shows a pronounced minimum very close to where it crosses the $4\text{CaO} \cdot \text{P}_2\text{O}_5 - 5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ eutectic trough of Behrendt and Wentrup (point A in Fig. 14(C)) and a pronounced maximum where it crosses the join $\text{CaO} - 5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ (point B). A second minimum lying within the field $\text{CaO} - 5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2 - 9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$ is followed by a still higher maximum extending over the range 60–70% $2\text{CaO} \cdot \text{SiO}_2$ —actually there is a slight rise in temperature from the first to the second of these compositions. This range begins close to the suggested $\text{CaO} - 9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$ join (point C) and includes the join $3\text{CaO} \cdot \text{SiO}_2 - 9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$ (point D). Incidentally, the phosphate solubilities of Blome's mixtures rose from about 50% for $4\text{CaO} \cdot \text{P}_2\text{O}_5$ alone to a maximum of over 80% at a composition in the neighbourhood of the $\text{CaO} - 9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$ join, which, on the whole, is consistent with the solubility data given above.

V.—THE SYSTEM IRON-OXYGEN.

The oxides of iron play such an essential part in the furnace reactions that they are perhaps the most significant of all the slag constituents. For an understanding of their behaviour in slags a knowledge of the stability relationships within the system iron-oxygen (of which metallic iron and its oxides can be considered as phases) is necessary. In studying oxide systems of this type the gaseous phase must be taken into account as a variable in addition to temperature and composition, as the oxygen pressure in the system exerts a determinative influence on the composition of the solid, or liquid, phase. Complete diagrammatic representation of such a system is possible only on a three-dimensional diagram on which temperature, pressure and composition can be simultaneously represented. Nevertheless, it is possible, and convenient, to construct a thermal equilibrium diagram of the usual kind to depict the stability relationships between the metal and its oxides in terms of temperature and composition only, neglecting pressure variations. The construction of such a diagram is fully justified on the ground of its practical utility, though it should be remembered that it is not complete in itself, and, further, that it does not correspond to any simple, plane section through the complete three-dimensional diagram.

* The location of the point X is, of course, unknown.

(a) *The Thermal Equilibrium Diagram.*

Data concerning the thermal equilibrium diagram of the system Fe-O can be obtained from a large number of published papers, but there is still considerable uncertainty about parts of the diagram, owing to lack of agreement between the observations of different workers. Attempts to construct a diagram have been made by Benedicks and Löfquist,⁽²⁾ by Pfeil,⁽⁷⁹⁾ by Mathewson, Spire and Milligan,⁽⁸⁰⁾ by H. Schenck and Hengler⁽⁸¹⁾ and by Vogel and Martin,⁽⁸²⁾ and full discussion of the experimental data utilised for the purpose will be found in the original papers by those authors. In addition, a review of the various diagrams proposed has been made by Pfeil and Winterbottom.⁽⁸³⁾ Fig. 15(A) is based mainly on the diagram proposed by Mathewson, Spire and Milligan. That part of the diagram relating to the partial system Fe_3O_4 - Fe_2O_3 has, however, been redrawn on the basis of data on the dissociation of Fe_2O_3 at high temperatures given by White, Graham and Hay⁽⁴⁴⁾ and by White,⁽⁸⁴⁾ which have enabled the limits of the solid solubility of Fe_2O_3 and Fe_3O_4 in one another to be fixed from 1200° to 1450° C. The melting temperatures of part of the Fe_3O_4 solid-solution range are also given and the existence of a eutectic is indicated. Sosman and Hostetter⁽⁸⁵⁾ had early postulated complete solubility between these two oxides at high temperatures, but this never gained wide acceptance, and Mathewson, Spire and Milligan, following Benedicks and Löfquist, showed partial solubility with a peritectic reaction between the two solid solutions at the melting point. The results of a re-investigation of the range Fe_2O_3 - Fe_3O_4 by Greig, Posnjak, Merwin and Sosman⁽⁸⁶⁾ agree with the diagram now reproduced, except that, according to those authors, the solubility of Fe_3O_4 in Fe_2O_3 is very small. The reason for this discrepancy is not clear, but it may be noted that Pfeil also obtained evidence of considerable solubility of Fe_3O_4 in Fe_2O_3 . According to White's data the melting point of oxide of the composition Fe_3O_4 should be about 1600° C. The four above-mentioned authors determined it to be 1591° C., but this was on the basis of the palladium melting point at 1549.5° C., and is subject to a correction of about +6° C.#. The melting points of Fe_2O_3 and of the eutectic between it and Fe_3O_4 must remain undetermined, for the dissociation pressures are so high at these temperatures that complete dissociation to the magnetite solid solution occurs below the melting point, even in an atmosphere of oxygen. Actually, an oxygen pressure of many thousands of atmospheres would be required to prevent this at 1600° C. The heavy broken line to the right of Fig. 15(A) shows the changes in composition that occur on heating Fe_2O_3 up to 1650° C. under an oxygen pressure of one atmosphere, the heating being carried out sufficiently slowly for equilibrium to be maintained throughout. Even at this oxygen pressure dissociation to the magnetite phase occurs at 1450° C. This is followed by further

loss of oxygen till 1560°C ., when melting occurs accompanied by a small but definite pick-up of oxygen. Further rise in temperature causes a further progressive loss of oxygen from the molten oxide as shown. It is of interest that 1565°C ., the earlier accepted figure for the melting point of Fe_2O_3 , was got by melting rapidly in an atmosphere of oxygen.⁽⁸⁷⁾ This method is inadequate to prevent

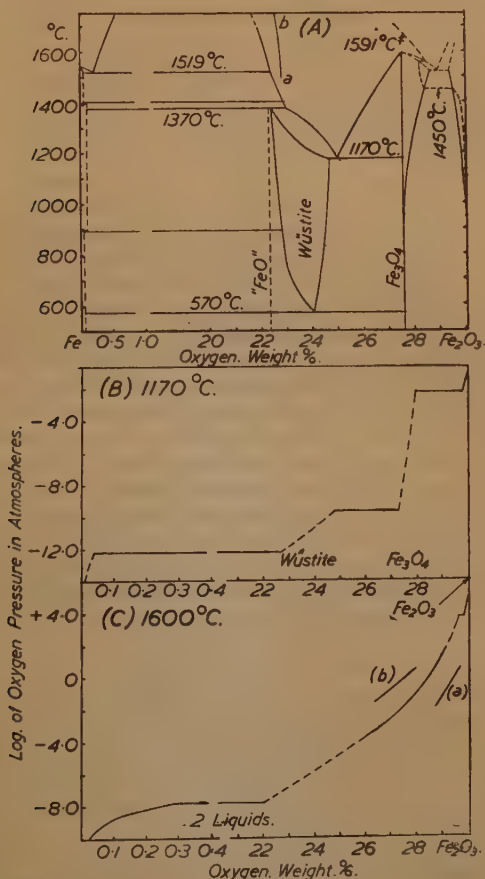


FIG. 15.—(A) Thermal Equilibrium Diagram of the System Iron-Oxygen (Mathewson, Spire and Milligan,⁽⁸⁰⁾ White, Graham and Hay,⁽⁴⁴⁾ Greig, Posnjak, Merwin and Sosman,⁽⁸⁶⁾ White⁽⁸⁴⁾). Curve (ab) shows results of Chipman and Fetters⁽¹⁸³⁾ (see Section V. (a), Addendum). (B) Variation of Oxygen Pressure with Composition in the System Iron-Oxygen at 1170°C . (C) Variation of Oxygen Pressure with Composition in the System Iron-Oxygen at 1600°C ; (a) Melt of liquid $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, (b) melt of $\text{Fe}_2\text{O}_3 + \text{SiO}_2$ (equimolecular proportions).

dissociation to the magnetite phase, for, though the transition from one phase to the other is sluggish at 1450°C. , it proceeds with ever-increasing rapidity as the temperature is raised above this value. Incidentally, the change-over is accompanied by an absorption of heat, which appears as an arrest during the taking of a heating curve of Fe_2O_3 , while a corresponding heat evolution is detectable on re-cooling the sample.⁽⁶⁵⁾

The fixing of the solid-solubility limits of the ferrous-oxide phase has caused considerable controversy. In Fig. 15(A) the homogeneity range is shown displaced entirely to the right of the composition FeO (22.27% oxygen). Mathewson, Spire and Milligan based the solubility limits shown mainly on the data of R. Schenck and his collaborators⁽⁸⁸⁾ derived from investigations on the equilibrium between the oxides of iron and the oxides of carbon at various temperatures. The placing of the homogeneity range in this manner agrees with the conclusions of Pfeil, and also with those of Jette and Foote,⁽⁸⁹⁾ who determined the solubility limits and measured the change in the lattice constant of the phase with changing oxygen content by means of X-rays. H. Schenck and Hengler⁽⁸¹⁾ and Vogel and Martin⁽⁸²⁾ also place the homogeneity range to the right of the composition FeO . There are, however, appreciable differences in the actual solubility limits indicated by these various workers. To distinguish the actual oxide phase from the hypothetical oxide FeO , R. Schenck suggested the name wüstite for it, and this has been generally adopted. There is general agreement that wüstite decomposes below about 570°C. into a eutectoid of Fe_3O_4 and metallic iron ("wüstite pearlite"), as shown by the intersection of the two solubility curves. The point of intersection appears in the various diagrams at compositions ranging from just over 23% to 24.0%. The reaction involved in the breakdown can probably be represented by the equation :



It is, however, a rather slow reaction, requiring fairly long periods of heating below 570°C. to reach completion, and it can be almost entirely suppressed by rapid cooling.^(90, 91) Its reversibility has also been established.⁽⁹¹⁾ The stable oxide in contact with metallic iron below 570°C. is magnetite; above this temperature wüstite is the stable phase.

There is considerable disagreement as to the form of the melting relationships over the range wüstite- Fe_3O_4 . Benedicks and Löfqvist concluded from the evidence then available that there was a eutectic between these two oxides, and indicated its probable temperature and composition as 1200°C. and 25.0% of oxygen approximately. Mathewson, Spire and Milligan also concluded that there was a eutectic in this range, and gave its temperature and composition as 1170°C. and 25.0% of oxygen. Both sets of authors concluded that wüstite in equilibrium with metallic iron melts

incongruently at 1370°C . with separation of iron and formation of a liquid phase richer in oxygen than the original wüstite. Pfeil, and Vogel and Martin, on the other hand, indicate a peritectic reaction occurring between wüstite and Fe_3O_4 at over 1400°C . and representing the lowest temperature of liquid formation in mixtures of the two oxides, while between wüstite and iron, close to the limit of homogeneity of the former, they show a eutectic melting at about 1370°C . H. Schenck and Hengler give a eutectic between wüstite and Fe_3O_4 but at a temperature of over 1300°C .

These discrepancies may be regarded as an indication of the practical difficulties involved in the study of this system, particularly in this composition range. Perhaps the chief difficulty is to find a crucible material that will not react unduly with the liquid oxide. The ordinary refractory oxides are ruled out for this reason. For the study of oxide compositions in equilibrium with iron, crucibles of that metal are an obvious choice and have proved satisfactory, while in dealing with the range Fe_3O_4 – Fe_2O_3 platinum or rhodium crucibles can be used. In the latter case some pick-up of metallic iron by the crucible material does occur, but is not serious (it is less with rhodium than with platinum), as the relatively high oxygen pressures involved tend to inhibit it. For the intermediate range between these two extremes, however, metallic iron cannot be used, as it would rapidly reduce the Fe_2O_3 content of the oxide till equilibrium was reached, while platinum, when used, acts in the opposite sense, picking up considerable amounts of iron and tending to raise the oxygen content of the melt. An added complication, always present, arises from the fact that changes in the composition of the oxide can also occur, owing to the pick-up or evolution of oxygen from, or to, the gas phase. For oxide compositions in the vicinity of wüstite it is satisfactory to employ an atmosphere as free from oxygen as can be obtained by chemical or other means to avoid oxidation, as, owing to the almost infinitesimal dissociation pressures of this oxide, the dissociation in any closed system will be negligible. Compositions containing appreciable ferric oxide, however, develop a measurable dissociation pressure at high temperatures, and will lose oxygen if the oxygen pressure is too low, just as they will gain oxygen if it is too high. Further, it is impossible in practice to maintain an atmosphere that will be in equilibrium with the original oxide composition at all temperatures, so that changes in composition will, in general, occur during heating and cooling. (One example of this has already been described.) Hence, the final composition got by analysis of a melt will not necessarily be the same as that for which arrests were recorded at higher temperatures. The ideal solution of this difficulty is to have the oxide enclosed in such a small space that any adjustments occurring between it and the gas phase will have a negligible effect on the composition, but this is somewhat difficult to arrange in practice. This method has, however, been used by

Greig, Posnjak, Merwin and Sosman⁽⁸⁶⁾ in studying compositions in the vicinity of Fe_3O_4 .

With regard to the utilisation of microstructures to throw light on relationships in the system, exact correlation with composition is possible, provided that the latter is determined on the sample as sectioned for micro-examination. Uncertainty arises, however, over the interpretation of some of the structures observed. Thus, the dispersion of iron globules observed with oxygen contents of 22-23% has been ascribed by Pfeil, and by Vogel and Martin to the presence of a eutectic between iron and wüstite, while Mathewson, Spire and Milligan attribute the presence of iron globules to the fact that the solubility of iron in the liquid oxide decreases with falling temperature. There is a similar lack of finality about the structures obtained in the wüstite- Fe_3O_4 range. In reproducing what is essentially the diagram of Mathewson, Spire and Milligan it is not the author's intention to claim ultimate authenticity for their proposals. It is worthy of note, however, that Bowen and Schairer,⁽³⁾ in a carefully carried-out investigation, have substantially confirmed their findings with regard to the composition of the liquid oxide in equilibrium with iron just above the temperature of the wüstite peritectic. The most accurate value of Bowen and Schairer for the composition of the liquid phase was 23.16% of oxygen at 1390° C., while that of Mathewson, Spire and Milligan was 23.00% at the peritectic temperature. These figures correspond to Fe_2O_3 contents of 11.56% and 9.5%, respectively. In view of the precautions taken by the former workers, their figure can probably be considered the more accurate. Again, the present author has himself had visible evidence of melting at just above 1200° C. in Fe_2O_3 -carbon mixtures adjusted to give compositions in the range wüstite- Fe_3O_4 after reaction at high temperatures. Only the fact that the Fe_2O_3 used was probably not of the highest purity prevents him from accepting this indication of the existence of a eutectic as conclusive.

Over most of the composition range from metallic iron to wüstite two immiscible liquids are formed on melting, one being liquid iron saturated with oxygen and the other a liquid oxide phase. The compositions of the liquids in equilibrium with each other are supposedly indicated by the boundary curves of the immiscibility zone, but the curve on the right, which refers to the oxide phase, has not yet been determined accurately. Mathewson, Spire and Milligan, however, have attempted to fix the course of the liquidus curve from the melting point of iron (the temperature of the monotectic horizontal in the presence of liquid oxide) to the temperature of the wüstite peritectic. They found that 2.20% of iron separated from liquid oxide in equilibrium with iron on cooling it from the former temperature to the latter. This, taken in conjunction with their determination of the liquid composition at the peritectic temperature, enabled them to place the composition of the end of the

monotectic horizontal at approximately 22.5% of oxygen, corresponding to a ferric-oxide content of 3.1%. Hence, apparently, appreciable Fe_2O_3 is present in the oxide phase in equilibrium with metallic iron right up to the melting point of iron. It will readily be seen that, at any temperature, molten iron oxide with a lower ferric-oxide content than that indicated by the liquidus curve at that temperature is incapable of existing. As pointed out by Bowen and Schairer,⁽³⁾ any attempt to decrease the ferric-oxide content below this value (*e.g.*, by chemical reduction) would result merely in the formation of metallic iron, leaving the composition of the oxide phase unaltered, though it would, of course, be decreased in amount. This agrees with Whiteley's conclusion⁽⁹²⁾ that a reversible equilibrium must exist in liquid iron-oxide melts that can be represented by the equation :



Reduction of the Fe_2O_3 in the oxide phase would simply cause this reaction to proceed from left to right till equilibrium was restored. The curve bounding the immiscibility zone on the left is, of course, the solubility curve of oxygen in liquid iron, attempts to determine which have been made by several investigators. Mathewson, Spire and Milligan based this part of their diagram on the oxygen-solubility determinations of Herty and his co-workers,⁽⁹³⁾ and took Tritton and Hanson's figure of 0.21% solubility at 1519° C., the temperature of the monotectic point.⁽⁹⁴⁾ Körber⁽⁹⁵⁾ has more recently determined the solubility of oxygen in liquid iron under molten FeO and FeO-MnO slags, expressing his results in terms of the partition coefficient of FeO between metal and slag. The partition coefficient, suitably expressed, should, of course, on theoretical grounds be numerically equivalent to the solubility. The curve drawn by Körber from a consideration of his own and Herty's results agrees fairly well with that of Herty, except that a rather lower solubility at temperatures over 1650° C. is indicated. Fig. 23(C), curve (a), shows Körber's curve for slags of this type drawn to a larger scale than Fig. 15(A). Hultgren and Phragmén⁽⁹⁶⁾ have criticised this curve on theoretical grounds, pointing out that it should be exponential in form, and on this basis they suggest that the monotectic composition should be about 0.24% of oxygen. (See Addendum on next page.)

Considerable uncertainty exists as to the solubility limits of oxygen in solid iron, and many different estimates of the solubility at both high and low temperatures have been made. A review of some of these has been given by Herty and Daniloff.⁽⁹⁷⁾ The limits indicated by Mathewson, Spire and Milligan are qualitative only, and were based mainly on the estimate by Tritton and Hanson⁽⁹⁴⁾ that the solid solubility was probably of the order of 0.05%. They also assumed that the solubility in γ -iron was somewhat higher than in the α and δ forms, and accordingly showed oxygen as lowering

slightly the α - γ change point and raising slightly the γ - δ change point. Vogel and Martin, and Schenck and Hengler, however, report an opposite effect on the change points. The latter workers show a decreasing solubility in α -iron with falling temperature below 900° C. in accordance with the findings of Krings and Kempens,⁽⁹⁸⁾ but this can hardly be said to be definitely established, though it is consistent with the view that oxygen can cause ageing effects in iron and mild steel. Larsen,⁽⁹⁹⁾ on the other hand, has given a solubility curve that shows a continuous decrease between the monotectic temperature and room temperature. (At the former temperature a solubility of about 0.05% is indicated.) His diagram gives no pointers as to the effects of oxygen on the allotropic change points, but his curve appears to indicate that a closed γ -loop may be formed. Such a loop has, according to Herty and Daniloff,⁽⁹⁷⁾ been postulated by Feszcezenko-Czopivsky and Orzechowsky.⁽¹⁹⁵⁾ Hultgren and Phragmén⁽⁹⁶⁾ also consider that the solubility in solid iron at the monotectic temperature is about 0.05%, but that at 1000° C. it is probably less than 0.01%. As more refined experimental methods become available, more accurate data should be forthcoming, and Sloman,⁽¹⁰⁰⁾ basing his estimate on the result of microscopic examination of slowly cooled samples in conjunction with oxygen determinations by the vacuum-fusion method, has recently stated that the low-temperature solubility in high-purity iron lies probably between 0.006% and 0.003%. He also found that a sample of his iron saturated at its melting point with FeO contained 0.15% of oxygen.

Addendum.—Since the above was written, Chipman and Fettters⁽¹⁸³⁾ have carried out a redetermination of the solubility of iron oxide in liquid iron from the melting point to approximately 1800° C. Like Herty and Körber, they used MgO crucibles, but found considerably lower solubilities than these earlier workers, the equation of their solubility curve being :

$$\text{Log (oxygen \%)} = -\frac{4860}{T} + 1.935.$$

They also determined the ferric-oxide/ferrous-oxide ratios in the iron-oxide layers in equilibrium with their iron melts over the same temperature range. Their curve, suitably recalculated, has been inserted in Fig. 15(A); the oxygen contents indicated are somewhat higher than those suggested by Mathewson, Spire and Milligan, whose experiments were carried out in iron crucibles. In the discussion that followed their paper, Darken pointed out that any MgO picked up from their crucibles by the oxide layer would displace the equilibrium in the direction of higher Fe_2O_3 , which agrees with ideas expressed later in the present paper. Darken stated that the true value of the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio at the melting point appeared to be about 0.055. This corresponds to approximately 22.65% of oxygen.

(b) *Oxygen-Pressure/Temperature/Composition Relationships.*

The oxygen-pressure/composition relationships within the system iron-oxygen at high temperatures can be described in general terms as follows: At any temperature each oxide exerts a definite oxygen pressure, which is a measure of its tendency to dissociate with evolution of oxygen and which increases approximately logarithmically with temperature. The reactions involved are strictly reversible and can be expressed in terms of equations of the type:



Generally, the higher the degree of oxidation represented by the oxide, the higher will be its dissociation pressure at any temperature. Thus, the dissociation pressures of Fe_2O_3 , Fe_3O_4 and FeO decrease in that order, provided that all three are stable at the temperature in question. In the case of solid- or liquid-solution ranges, where continuous variation of a given phase is possible, the oxygen pressure varies continuously with the composition, increasing progressively with the oxygen content. When there is immiscibility in the solid or liquid states, two unchanging saturated phases co-exist throughout the entire range of immiscibility, and there is, at a given temperature, only one characteristic oxygen pressure with which they are both simultaneously in equilibrium. Hence, at a constant temperature the dissociation pressure of oxide compositions lying within a range of immiscibility is constant and independent of composition within the limits of the immiscibility. These relationships will be made clearer by reference to Figs. 15(B) and 15(C), which show how the dissociation pressure (plotted as the logarithm of the pressure) varies with composition across the iron-oxygen diagram, (B) for the solid oxides at 1170°C. , and (C) for the liquid oxides at 1600°C. In the former case a "stepped" curve is obtained with three horizontal sections corresponding to the three immiscibility ranges between oxygen-saturated iron and wüstite, wüstite and magnetite, and magnetite and ferric oxide. The limits of the horizontals correspond to the solubility limits of the appropriate phases in each case. The four sloping portions of the curve correspond to the four solid-solution ranges, namely, wüstite (or oxygen) in solid iron, the wüstite range, the magnetite range and the ferric-oxide range. In Fig. 15(C) the horizontal section on the left corresponds to the range over which two immiscible liquids co-exist. A very short horizontal section towards the right-hand end of the curve is rendered necessary by the fact that 1600°C. is not above the melting point of pure Fe_2O_3 . Over the rest of the range the melts will consist of a single, homogeneous phase, and the oxygen pressure varies continuously with composition.

In any system containing an iron oxide dissociation will in theory occur when the oxygen pressure is lower than the dissociation pressure of the oxide at the temperature within the system, and

equilibrium will not be attained until the oxide has dissociated to such an extent that the dissociation pressure of the altered oxide is equal to the pressure in the system. Conversely, combination with oxygen occurs if the oxygen pressure is higher than the dissociation pressure of the oxide (provided that it is not already in its highest possible state of oxidation). Dissociation pressures over the composition range iron to Fe_3O_4 are, however, too low at all ordinarily attainable temperatures to be measured directly (that of wüstite is about 10^{-8} atmospheres at 1600°C.). Hence, they can only be estimated indirectly, *e.g.*, from thermo-chemical data, or from data concerning the equilibria between the oxides and a gaseous phase consisting of mixtures of CO and CO_2 , or of hydrogen and H_2O . Investigations of these latter equilibria have been carried out by several investigators.^(88, 101-103) Their curves showing the variation in the equilibrium CO/CO_2 , or $\text{H}_2/\text{H}_2\text{O}$, ratio with oxide composition are stepped in the manner of Fig. 15(B), and are of an analogous nature, since equilibrium is attained only when the dissociation pressure of the oxide is equal to the partial pressure of oxygen in the gaseous phase. In the case of the oxides of carbon this is dependent on the reversible gaseous equilibrium :



for which the equilibrium constant is :

$$K = \frac{(\text{CO})^2 (\text{O}_2)}{(\text{CO}_2)^2}.$$

The equilibrium ratio of CO to CO_2 is thus directly dependent on the oxygen pressure of the system, which is, in turn, equal to the oxygen pressure of the oxide. The latter can obviously be calculated, provided that K is known, and the ratio CO/CO_2 is measured experimentally. K is obtainable from thermo-chemical data. Attempts to estimate the dissociation pressures of the oxides of iron by such methods have been made by Matsubara,⁽¹⁰¹⁾ McCance,⁽¹⁰⁴⁾ Tigerschiöld⁽¹⁰⁵⁾ and others. Some uncertainty is introduced, however, with regard to the application of such calculations to steel-making temperatures, in that the calculation of values round about 1600°C. is dependent on the extrapolation of data generally obtained below 1000°C. Another complication arises owing to the formation of solid solutions between the oxides at high temperatures. (In the case of Fe_2O_3 , where it is possible to compare the calculated values with the results of experiment, the former have generally been decidedly low.)

Over the composition range Fe_3O_4 - Fe_2O_3 approximately, the dissociation pressures are capable of direct measurement from roughly 1100°C. upwards. Studies of this part of the system iron-oxygen have been made by a number of workers^(106, 85, 44, 107-110, 86, 84) and include determinations on both the liquid and solid oxides. The variation of oxygen pressure with composition across the range

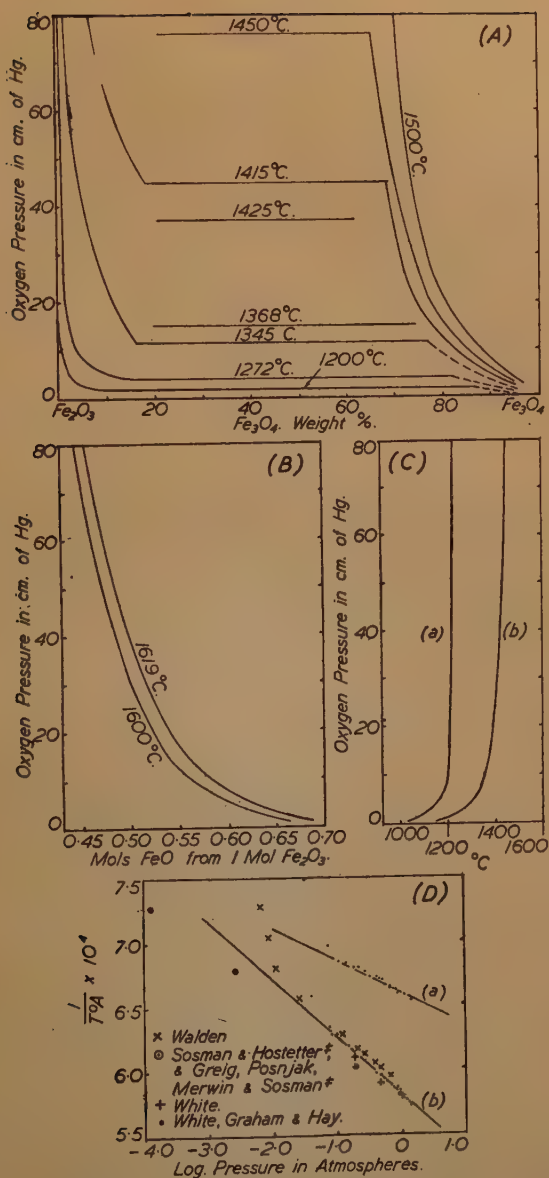


FIG. 16.—(A) Dissociation-Pressure/Composition Isotherms of the System Fe_2O_3 – Fe_3O_4 (White, Graham and Hay,⁽⁴⁴⁾ White⁽⁸⁴⁾). (B) Dissociation-Pressure/Composition Isotherms of Liquid Iron Oxide (White⁽⁸⁴⁾). (C) Dissociation-Pressure/Temperature Curves, (a) initial dissociation pressures of Fe_2O_3 , (b) dissociation pressures of Fe_2O_3 saturated with Fe_3O_4 (White, Graham and Hay⁽⁴⁴⁾). (D) Dissociation-Pressure/Temperature Data, (a) initial dissociation pressures of Fe_2O_3 , (b) dissociation pressures of Fe_2O_3 saturated with Fe_3O_4 .

Fe_2O_3 - Fe_3O_4 at various temperatures, as indicated by the data of White, Graham and Hay⁽⁴⁴⁾ and of White,⁽⁸⁴⁾ is shown in Fig. 16(A), in which the incomplete pressure/composition isotherms of the former authors (Fig. 6 of their paper) have been completed as far as possible from the additional data provided by Figs. 2 to 4 of the latter author's paper. On the whole the agreement between the data contained in the two papers is reasonably good, though a discrepancy will be noticed between the isotherms at 1415°C . (White, Graham and Hay) and at 1425°C . (White). Fig. 16(B) shows similar curves for the liquid oxides as determined by White. In the latter case, to avoid making assumptions as to the possible stability of Fe_3O_4 in the liquid state, the composition was expressed simply in terms of the total ferrous-oxide content formed at equilibrium in a melt consisting originally of 1 gram-molecule of Fe_2O_3 . The curves of Fig. 16(B) are smooth, indicating complete miscibility over the range studied.

Fig. 16(A) shows the rapid drop in dissociation pressure that accompanies the solution of Fe_3O_4 in Fe_2O_3 . Because of this it is a matter of some difficulty to determine the initial dissociation pressure of magnetite-free Fe_2O_3 . In this connection Greig, Posnjak, Merwin and Sosman⁽⁸⁶⁾ pointed out that studies of the magnetic transformations in Fe_2O_3 ^(111, 112) indicate the presence of small but definite traces of Fe_3O_4 at all temperatures over 650°C . If, however, the temperatures at which oxygen loss from the oxide is first observed at various oxygen pressures are plotted against those pressures the curve obtained can be considered as approximating to that of the dissociation pressure of magnetite-free Fe_2O_3 . Curve (a) of Fig. 16(C) was obtained in this fashion; curve (b) shows the variation with temperature of the dissociation pressure of the two saturated solid solutions. Both are taken from the paper by White, Graham and Hay. Determinations of equilibrium pressures on curve (b) are to be found in several of the other papers to which reference has been made above, and in Fig. 16(D) the results of the more comprehensive of these investigations have been plotted. With regard to the discrepancies revealed, it is unlikely that the deviations from the linear at lower pressures and temperatures found by Walden and by White, Graham and Hay have any practical significance. They are probably due to gas leakage through, or liberation of gases from, the refractory tubes employed at these low pressures. Neglecting these deviations, the results of these workers lie on approximately parallel lines, which suggests that the differences observed may be mainly due to differences in the temperature scales employed. Walden gave no particulars of the calibration of his thermocouple, so his scale is unknown. White, Graham and Hay, and White used a scale based on the temperatures 1063°C . for the melting point of gold, and 1555°C . for that of palladium (though this is not stated in their original papers). Sosman and Hostetter,⁽⁸⁵⁾ and Greig, Posnjak, Merwin and Sosman used the Geophysical Scale.

The points attributed to Sosman and Hostetter are approximate only, as no strictly horizontal portions occur on their pressure/composition isotherms at 1100° and 1200° C. Pressures of about 0.1 and 2.0 mm. of mercury are indicated, however, the latter of which has also been accepted as an approximate value by Greig, Posnjak, Merwin and Sosman. The broken line through these two values and the values obtained by the last-named authors approach the line through White, Graham and Hay's values at an oxygen pressure of about 1 atm. At the present time it is perhaps hardly justifiable to draw a mean curve through the various experimental points. For one thing, appreciable curvature due to solid-solution formation is possible. The most painstaking studies, however, have

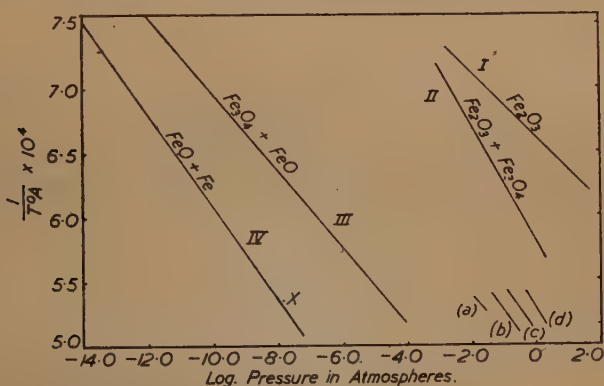


FIG. 17.—Dissociation-Pressure/Temperature Relationships in the System Iron-Oxygen.

undoubtedly been those of Sosman and his co-workers, who used very prolonged periods of heating, and approached equilibrium from both higher and lower states of oxidation. Even apart from this, the most likely error in determining the equilibrium by the measurement of gas pressures is that too high a pressure should be obtained owing to gas leakage, pick-up of iron by the platinum crucibles, &c.

Curve (a) of Fig. 16(D) is a replot of curve (a) of Fig. 16(C), showing the original experimental points of White, Graham and Hay.

In Fig. 17 the complete pressure/temperature relationships of the system iron-oxygen, as indicated by the data at present available, are shown. The FeO and Fe₃O₄ dissociation-pressure curves are based on recent thermal data on the CO/CO₂ and H₂/H₂O equilibria at high temperatures as quoted by Chipman.⁽¹¹³⁾ Certain additional data have also been plotted on this diagram. Thus, Chipman⁽¹¹³⁾ and Fontana and Chipman⁽¹¹⁴⁾ have studied the equilibrium between liquid iron containing oxygen and H₂/H₂O mixtures. On

the basis of the amended data given in the second of these papers the dissociation pressure of liquid FeO (or, more accurately, of the liquid oxide phase in equilibrium with liquid iron containing oxygen) at 1600° C. is as indicated by the point X, which is only a little higher than that got by extrapolation of the data for the solid oxide as indicated by curve IV. Curves (a), (b), (c) and (d) are as indicated by the work of White for liquid oxide of the compositions 100% Fe₃O₄, 90%-Fe₃O₄/10%-Fe₂O₃, 80%-Fe₃O₄/20%-Fe₂O₃ and 70%-Fe₃O₄/30%-Fe₂O₃. There is a considerable discrepancy between the calculated value for the dissociation pressure of Fe₃O₄ and that shown by curve (a). In the author's opinion, the experimentally determined pressures are almost certainly too high, in spite of the attempt made to apply a correction for the effect of iron pick-up by the platinum crucibles, which would, of course, be increasingly marked the lower the oxygen pressure. (Krings and Schackmann⁽¹¹⁰⁾ indicate even higher pressures than those shown.) Some of the discrepancy between the experimental values and curve III., however, is probably to be attributed to the fact that the latter was deduced from data relating to magnetite in equilibrium with wüstite and possibly containing some FeO in solid solution. Though no such solubility was indicated by Mathewson, Spire and Milligan in their diagram (Fig. 15(A)), Pfeil⁽⁷⁹⁾ concluded that there was solubility and Schenck and Hengler⁽⁸¹⁾ and Vogel and Martin⁽⁸²⁾ came to the same conclusion. Further indications of this are also given by the reduction isotherms of Matsubara,⁽¹⁰¹⁾ Eastman and Evans,⁽¹⁰²⁾ &c.

The curves of Figs. 15(B) and 15(C) are based on data contained in Figs. 15(A), 16(A), (B), (C) and (D), and 17, with the exception of that part of curve 15(C) which concerns the pressures of oxygen solutions in liquid iron. This is based on the data of Chipman and Fontana.

A useful critique and review of the data then available on the system Fe-O was published in 1929 by Ralston.⁽¹¹⁵⁾

VI.—EQUILIBRIUM IN THE SYSTEM IRON-OXYGEN IN THE PRESENCE OF OTHER OXIDES.

The influence of foreign oxides on equilibria between the phases of the system Fe-O is of importance because of its bearing on the behaviour of iron oxides in slags. Data concerning the relevant systems are, however, very incomplete as yet, for the experimental difficulties involved in their study are considerable, and it is only by correlation of data from, in some cases, widely different sources that a deduction of the probable relationships involved can be made. In this connection the work of R. Schenck and his collaborators^(88, 89, 116, 117) on iron-oxide reduction equilibria in the presence of other oxides at 800° and 900° C. has been found particularly informative, even though this method of study has been found to

possess a certain degree of fallibility (*e.g.*, as revealed by the work of those authors on the solubility of oxygen in solid iron).

Dissociation-pressure/composition relationships in three component systems are necessarily more complex than in the simple binary system Fe—O. In a ternary system at constant temperature, variation in the dissociation pressure with composition is possible when either one or two solid (or liquid) phases are present. Only when three such phases co-exist (*i.e.*, four phases, counting the gas phase) is the dissociation pressure independent of composition (when the equilibrium gas phase is a CO—CO₂ mixture this is shown by the constancy of the composition of the gas phase). Thus, for instance, the dissociation pressure of a solid solution of Fe₃O₄ in FeO.Al₂O₃ (see Fig. 20(D)) will increase continuously as the ratio of Fe₃O₄ to FeO.Al₂O₃ is increased at constant temperature, assuming that no immiscibility gap in the series intervenes. Similarly, when the composition is such that two solid phases are present—say, conjugate compositions of the Fe₂O₃—Al₂O₃ and the Fe₃O₄—FeO.Al₂O₃ series—then, as the proportion of iron oxides in the system is increased at constant temperature, the compositions of both solid solutions alter and the dissociation pressure will increase. Variation of the composition along a line joining conjugate compositions of two solid-solution series (*i.e.*, in such a way that the compositions of the two phases are unaltered and only their relative amounts vary) is, however, possible without change in the dissociation pressure. When three solid phases co-exist, as in the various ternary fields of Fig. 19(A), the composition can be varied in any direction at constant temperature without change in the dissociation pressure, so long as the limits of the particular field are not crossed, in which case one of the three phases would, of course, disappear, and a new phase would appear whenever a new ternary field was entered, resulting in a new constant value of the dissociation pressure.

According to Schenck's reduction curves the dissociation pressures of the iron oxides and iron-oxide-containing compounds occurring in his samples decrease in the order Fe₂O₃, MgO.Fe₂O₃, CaO.Fe₂O₃,* MnO.Fe₂O₃, Fe₃O₄ (in equilibrium with wüstite), CaO.Fe₃O₄, wüstite (in equilibrium with oxygen-saturated iron), 2CaO.Fe₂O₃, 2FeO.SiO₂ and FeO.Al₂O₃. The various solid-solution series have dissociation pressures varying continuously between those of the end-members of the series as indicated above. Roberts and Merwin⁽⁴⁵⁾ found that dissociation of the Fe₂O₃ in MgO.Fe₂O₃ began in air at as low a temperature as 1000° C., while White, Graham and Hay⁽⁴¹⁾ concluded that neither of the calcium ferrites has a measurable dissociation pressure below its melting point. Study of the phase distributions in the systems discussed below shows that

* Actually, it is not absolutely certain from Schenck's data whether MgO.Fe₂O₃ or CaO.Fe₂O₃ has the higher dissociation pressure, though, from the fact that calcium is the more electropositive ion, it might be expected that CaO.Fe₂O₃ would have the higher stability.

there is a direct relationship between the "stabilities" of these various constituents and their dissociation pressures. The phase distribution at equilibrium in any system is, of course, determined by the necessity for the attainment of minimum free energy in the system under any conditions of temperature, pressure and composition. The significance of dissociation pressure in this connection can be shown, in somewhat simplified fashion, as follows :

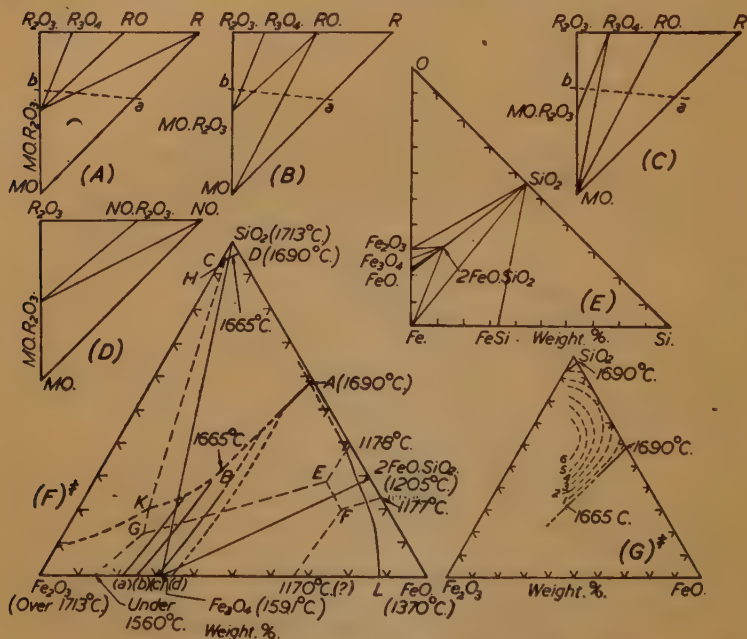


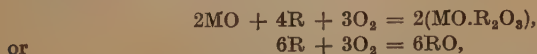
FIG. 18.—(A) to (C) Possible Phase Distributions of the System R-O-MO. (D) Phase Distribution in the System MO-NO- R_2O_3 when the dissociation pressure of $NO.R_2O_3$ exceeds that of $MO.R_2O_3$. (E) Phase Relationships in the System Fe-Si-O (Kanz, Scheil and Schultz⁽¹¹⁸⁾). (F) Liquidus Surface (tentative) and Oxygen-Pressure/Composition Relationships at 1619° C. of the System FeO- Fe_2O_3 - SiO_2 . (G) Effect of Al_2O_3 on the Immiscible-Liquid Zone of the System FeO- Fe_2O_3 - SiO_2 (Greig⁽⁶⁾).

Consider the system R-O-MO at temperature T , where R is a metal forming the oxides RO, R_3O_4 and R_2O_3 having dissociation pressures P^I , P^{II} and P^{III} at T such that $P^I < P^{II} < P^{III}$, and where MO is a "stable" oxide of lower dissociation pressure than P^I . Consider, further, that the compound $MO.R_2O_3$ of dissociation pressure P^{IV} higher than that of MO occurs. It is assumed that T is below the temperature of liquid formation in the system, which is essentially similar in type to the systems containing iron oxides and a foreign basic oxide studied by Schenck and his co-workers, except

that, for simplicity, it will be assumed that there is negligible solid solubility between the various phases. Figs. 18(A), 18(B) and 18(C) show the phase distributions that may occur in the system thus defined. They represent simply the various modes in which the system can be made to conform with the phase rule, without taking account of the relative stabilities of the various phases. Now consider the system to be isolated and to contain the amounts 2MO, 6R and $4\frac{1}{2}\text{O}_2$ (which are convenient for the purpose in view), where the chemical symbols represent the molecular weights of the substances. If no oxidation of R occurs, as will be the case if the oxygen pressure of the system is kept low enough, the composition of the solid part of the system will be as represented by the point (a) in the above-mentioned diagrams, while (ab) will be the path along which the composition changes as combination of R with oxygen occurs. Suppose the oxygen pressure to be raised by decreasing the volume of the system. At any pressure P^x , if no combination with oxygen occurs :

$$F_1^x = F_{2\text{MO}}^x + F_{6\text{R}}^x + 4\frac{1}{2}F_{\text{O}_2}^x,$$

where F_1^x is the Gibbs free energy of the system at the pressure P^x , and $F_{2\text{MO}}^x$, $F_{6\text{R}}^x$, $4\frac{1}{2}F_{\text{O}_2}^x$ represent the free energies of the amounts 2MO, 6R and $4\frac{1}{2}\text{O}_2$ at pressure P^x . Now, according to the diagrams, oxidation can take place initially in either of two ways, viz., according to the equations :



the former corresponding to the relationships indicated in Fig. 18(A), and the latter to those in Figs. 18(B) and 18(C). The former will occur reversibly at a pressure P^{IV} , since, as defined above, $\text{MO} \cdot \text{R}_2\text{O}_3$ will have the highest dissociation pressure in the phase field $\text{MO}-\text{R}-\text{MO} \cdot \text{R}_2\text{O}_3$; the latter at pressure P^{I} , since RO has the highest dissociation pressure in the field $\text{MO}-\text{R}-\text{RO}$. If each reaction occurs reversibly at its own equilibrium pressure, there will be no change in the Gibbs free energy, and hence we can write :

$$\begin{array}{l} \text{and} \qquad \qquad \qquad F_{2\text{MO}}^{\text{IV}} + F_{4\text{R}}^{\text{IV}} + 3F_{\text{O}_2}^{\text{IV}} = F_{2(\text{MO} \cdot \text{R}_2\text{O}_3)}^{\text{IV}} \\ \qquad \qquad \qquad \qquad \qquad F_{6\text{R}}^{\text{I}} + 3F_{\text{O}_2}^{\text{I}} = F_{6\text{RO}}^{\text{I}}, \end{array}$$

following the same convention as to symbols as was described above. However, over the pressure ranges involved, the changes of free energy of the solid phases with pressure will be negligible relative to those of the gas phase. Hence, the free energies of the solids can be considered independent of pressure, and the pressure symbols can be dispensed with in those terms which refer to solid phases. Hence we can write :

$$\begin{array}{l} F_2^x = F_{2(\text{MO} \cdot \text{R}_2\text{O}_3)} + F_{2\text{R}} + 1\frac{1}{2}F_{\text{O}_2}^x, \\ \qquad \qquad \qquad = F_{2\text{MO}} + F_{6\text{R}} + 3F_{\text{O}_2}^{\text{IV}} + 1\frac{1}{2}F_{\text{O}_2}^x, \\ \text{and} \qquad \qquad \qquad F_3^x = F_{2\text{MO}} + F_{6\text{RO}} + 1\frac{1}{2}F_{\text{O}_2}^x, \\ \qquad \qquad \qquad = F_{2\text{MO}} + F_{6\text{R}} + 3F_{\text{O}_2}^{\text{I}} + 1\frac{1}{2}F_{\text{O}_2}^x, \end{array}$$

where F_2^X and F_3^X represent the free energies of the system at pressure P^X at the completion of the first and second modes of oxidation, respectively.

Hence:

$$F_1^X - F_2^X = 3(F_{O_2}^X - F_{O_2}^{IV}) = 3RT \ln \frac{P^X}{P^{IV}},$$

$$F_1^X - F_3^X = 3(F_{O_2}^X - F_{O_2}^I) = 3RT \ln \frac{P^X}{P^I},$$

$$F_2^X - F_3^X = 3(F_{O_2}^{IV} - F_{O_2}^I) = 3RT \ln \frac{P^{IV}}{P^I}.$$

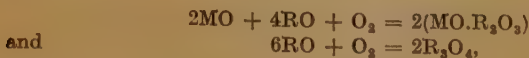
The necessary condition for any reaction to occur is that it should be accompanied by a decrease in the free energy of the system. Further, where more than one reaction is possible, that will occur which will be accompanied by the greatest decrease of free energy. Hence, it will be seen, first, that P^X must be greater than at least one of the pressures P^{IV} and P^I , and, secondly, that F_2^X will represent the lowest free energy attainable if $P^I > P^{IV}$, while F_3^X will represent the lowest free energy attainable if $P^{IV} > P^I$. In the former case the join $MO.R_2O_3-R$ will occur in the phase diagram; in the latter case the join $MO-RO$ will occur. Hence in the solid state the reaction:



will proceed to completion, to the right in the first case and to the left in the second. A species of "self-oxidation" of the oxide RO in the presence of MO occurs in the former case.

If the join $MO.R_2O_3-R$ occurs in the phase diagram, the phase distribution over the rest of the composition range is fixed automatically as shown in Fig. 18(A), and progressive raising of the oxygen pressure will result in oxidation of the remaining metal R to RO, then to R_3O_4 and then to R_2O_3 , each step representing a lowering of the free energy of the system at all pressures higher than the corresponding equilibrium pressure.

If the join $MO-RO$ occurs there are again two ways in which further oxidation can occur, these being represented by the equations:



corresponding to the relationships shown in Figs. 18(B) and 18(C), respectively, and reversible at pressures P^{IV} and P^{II} , respectively. The free energy of the system at pressure P^X at the completion of these reactions will be given by:

$$\begin{aligned} F_4^X &= F_{2(MO.R_2O_3)} + F_{2(RO)} + \frac{1}{2}F_{O_2}^X, \\ &= F_{2MO} + F_{6RO} + F_{O_2}^{IV} + \frac{1}{2}F_{O_2}^X, \\ &= F_{2MO} + F_{6R} + 3F_{O_2}^I + F_{O_2}^{IV} + \frac{1}{2}F_{O_2}^X \end{aligned}$$

in the first case, and :

$$\begin{aligned} F_5^x &= F_{2MO} & + F_{2R_2O_3} & + \frac{1}{2}F_{O_2}^x, \\ &= F_{2MO} & + F_{6RO} & + F_{O_2}^{II} + \frac{1}{2}F_{O_2}^x, \\ &= F_{2MO} & + F_{6R} & + 3F_{O_2}^I + F_{O_2}^{II} + \frac{1}{2}F_{O_2}^x \end{aligned}$$

in the second case. Hence :

$$\begin{aligned} F_3^x - F_4^x &= F_{O_2}^x - F_{O_2}^{IV} = RT \ln \frac{P^x}{P^{IV}}, \\ F_3^x - F_5^x &= F_{O_2}^x - F_{O_2}^{II} = RT \ln \frac{P^x}{P^{II}}, \\ F_4^x - F_5^x &= F_{O_2}^{IV} - F_{O_2}^{II} = RT \ln \frac{P^{IV}}{P^{II}}. \end{aligned}$$

Hence, $MO.R_2O_3$ will be formed if $P^{II} > P^{IV}$, provided that $P^x > P^{IV}$, while R_3O_4 will be formed if $P^{IV} > P^{II}$, provided that $P^x > P^{II}$. In the former case the join $MO.R_2O_3-RO$ will occur (Fig. 18(B)), while in the latter the join $MO-R_3O_4$ will occur (Fig. 18(C)).

In both cases the remaining join in the system, $MO.R_2O_3-R_3O_4$, is inevitable. (If, however, $P^{IV} > P^{III}$ this join would not occur, as $MO.R_2O_3$ would not be formed, but as it has already been postulated that this compound does occur, this case need not be considered.)

Summarising, the distribution shown in Fig. 18(A) occurs if $P^{III} > P^{II} > P^I > P^{IV}$, that of (B) occurs if $P^{III} > P^{II} > P^{IV} > P^I$, and that of (C) if $P^{III} > P^{IV} > P^{II} > P^I$. In all three cases, in traversing the oxidation path (*ab*) from (*a*) to (*b*), i.e., in the direction of increasing oxidation, the equilibrium pressure rises progressively in a series of steps. This is a necessary condition, following directly from the relationships just discussed, and provides a useful criterion that can be applied to the construction of pressure-composition diagrams of such systems. Of course, solid solubility is a complicating factor in the actual iron-oxide systems, and one the effect of which can hardly be computed. Nevertheless, the same general relationships should hold.

By similar methods it can be shown that the phase distribution in systems of the type $MO-NO-R_2O_3$, where both MO and NO form compounds of the ferrite type with R_2O_3 , is dependent on the relative dissociation pressures of the compounds. Thus, Fig. 18(D) shows the phase distribution to be expected in such a system when the dissociation pressure of $NO.R_2O_3$ exceeds that of $MO.R_2O_3$. There is a join from $MO.R_2O_3$ to NO , and hence the reaction :



proceeds to the right in the solid state.

(a) The System Fe-Si-O.

Fig. 18(E) shows the phase relationships in the system Fe-Si-O as given by Kanz, Scheil and Schulz⁽¹¹⁸⁾ to explain their observations

on the microstructure of a series of iron-oxide/silica melts. It was derived primarily, however, from a consideration of Schenck's reduction curves for a series of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ mixtures at 900°C .⁽¹¹⁶⁾ the breaks in these curves being assumed to correspond with the boundaries of phase fields. It thus purports to show relationships in fully solidified slags. Joins are shown running from 2FeO.SiO_2 to both Fe_3O_4 and Fe_2O_3 . There is some doubt concerning the authenticity of the latter join, however, for Fe_3O_4 has been found in iron-oxide/ SiO_2 slags lying in the field $\text{Fe}_2\text{O}_3\text{-}2\text{FeO.SiO}_2\text{-SiO}_2$ of Fig. 18(E) (see Benedicks and Löfquist,⁽²⁾ pp. 92 *et seq.*), and in silica bricks taken from the roofs of open-hearth furnaces, both acid and basic.^(119, 120) In such bricks, as far as the zones in the neighbourhood of the hot face are concerned, the iron oxide would presumably be a constituent of a liquid matrix which could hardly be far removed from equilibrium with solid SiO_2 , and magnetite could not separate from such a liquid on the basis of the phase distribution shown unless it did so as a metastable phase at temperatures too high for the crystallisation of Fe_2O_3 on account of its high dissociation pressure. Again, McGaughey⁽¹²¹⁾ has described the decomposition of fayalite into SiO_2 and Fe_3O_4 on heating in air. The present author has himself observed that SiO_2 appears to have little or no effect on the dissociation of Fe_2O_3 over the range $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ so long as no liquid formation occurs. All these observations are consistent with the phase distribution shown in Fig. 18(F). Incidentally, it is probably significant that the free-energy relationships deduced from the relative dissociation pressures of the various phases as indicated by Schenck's data give the latter phase distribution as the more stable one. Of course, this neglects the possible effects of solid-solution formation between the phases involved.*

Knowledge of melting relationships in this system is still very incomplete. In Fig. 18(G), however, an attempt has been made to depict relationships at the liquidus surface of the important partial system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$ on the basis of the experimental evidence available and in the light of the phase relations just discussed. *AB* shows the outer limit of the biliquidal zone at the temperatures of immiscible liquid formation as indicated by the work of Greig.⁽⁵⁾ The other limit is shown by a short line *CD* near the SiO_2 corner of the diagram. The temperature along *AB* drops, probably con-

* In the discussion of the recent "Co-operative Investigation on the Factors Influencing the Durability of the Roofs of Basic Open-Hearth Furnaces" by Swinden and others,⁽¹²⁰⁾ the author pointed out that the finding of magnetite in roof bricks was inconsistent with the phase diagram for the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ proposed by Hay and White.⁽¹²²⁾ The reason for the discrepancy was that the latter authors, on the basis of the above-mentioned papers by Schenck and his co-workers and by Kanz, Scheil and Schulz, assumed the existence of the tie $2\text{FeO.SiO}_2\text{-Fe}_2\text{O}_3$ in the system Fe-Si-O . Fig. 18(F), however, and the modified phase diagram of the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ given later in the present paper are quite consistent with the occurrence of Fe_3O_4 in used silica bricks.

tinuously (though there is a considerable gap in Greig's results, as shown by the broken portion between *A* and *B*), from 1689° C.# at *A* to 1665° C.# at *B*. Fe_2O_3 , therefore, actually lowers the temperature of immiscible-liquid formation in iron-oxide/ SiO_2 slags, but markedly increases the width of the immiscibility zone. In its practical implications the latter effect seems to outweigh the former. Thus iron oxide is not so destructive of silica refractories under oxidising as under reducing conditions, *e.g.*, silica roof bricks can carry more iron oxide without dripping under oxidising than under reducing conditions. From *AB* the liquidus surface slopes steeply towards the low-melting region of the diagram, mainly confined to the composition range containing over 50% of FeO . Binary eutectic troughs running from the two binary eutectics of the FeO - Fe_2O_3 system and the two of the FeO - SiO_2 system should meet in three quintuple points. The exact location of these is unknown, but it is probable that the lowest-melting compositions occur with fairly low Fe_2O_3 contents, for progressive oxidation of FeO - SiO_2 melts soon produces a rise in the melting point. Observations on such melts suggest that the lowest melting temperature is under 1100° C. Hence, the ternary eutectics *E* and *F* of Fig. 18(*F*) will probably melt at about that temperature and will be expected to lie fairly close to the line of the FeO - SiO_2 binary system. The third quintuple point *G* may, or may not, lie within the field Fe_2O_3 - Fe_3O_4 - SiO_2 .* It has probably a considerably higher melting point than the other two, as melts lying within this field are relatively infusible. As indicated below in discussing the system CaO - FeO - Fe_2O_3 - SiO_2 , its melting point is probably at least in excess of 1388° C.# As previously indicated (see Fig. 13(*A*)), the binary eutectic of the system Fe_2O_3 - SiO_2 must be situated close to the SiO_2 end of the diagram. Hence, the corresponding binary eutectic trough of the ternary system must pass through the bi-liquidal zone in the form of a straight line (*HK* of Fig. 18(*F*)) joining two conjugate liquid compositions, and will represent a minimum temperature in the surface of immiscible-liquid formation. In actual fact there will be two surfaces dipping towards, and intersecting along, this line. If the drop from *A* to *B* is continuous, it follows that *K* must lie somewhere to the left of *B*. The continuation of *HK* will run into the ternary eutectic *G*.

Curve *LA* of Fig. 18(*F*) calls for comment. As previously pointed out, the system FeO - SiO_2 is not a true binary system, owing to the peritectic dissociation of FeO . Bowen and Schairer,⁽³⁾ during their investigation of the "binary" system, found that all of their melts contained appreciable amounts of Fe_2O_3 after quenching from the liquidus temperatures or higher, in spite of the fact that melting was carried out in iron crucibles and in an atmosphere of nitrogen from which the oxygen had been carefully removed.

* Relationships in the quaternary system CaO - SiO_2 - Fe_3O_4 - Fe_2O_3 - SiO_2 , which are discussed later, suggest that it is a eutectic point.

Curve *LA* shows the actual compositions of their melts. The Fe_2O_3 content decreases progressively from 11.56% for pure FeO to 2.25% (about 3.2% of the iron-oxide content) for a melt of fayalite composition, while with higher SiO_2 contents it decreases still further to roughly 2% for a melt containing 43.5% of SiO_2 . An investigation of the effect was made by those authors and they concluded that the liquidus surface of the Fe-Si-O ternary system corresponding to equilibrium between liquid silicate and metallic iron overlapped the FeO- SiO_2 join. The curve shown represents compositions on that surface at the temperatures at which solid slag first starts to freeze—the so-called liquidus curve of the “binary” system—and therefore indicates compositions in equilibrium with metallic iron at these temperatures. Hence, liquid oxide compositions to the right of *LA* are unrealisable at these temperatures, it being impossible to reduce the Fe_2O_3 content to lower figures. Further, fayalite as well as free FeO should dissociate on melting to give metallic iron and a melt containing the equilibrium amount of Fe_2O_3 . Bowen and Schairer succeeded in demonstrating this separation of iron at the melting point of fayalite. They also studied the effect of temperature on the Fe_2O_3 content of melts with SiO_2 contents ranging from 20% to 36%, and found little or no decrease in the Fe_2O_3 contents with temperature over the range from 1215° to 1500° C. From this they concluded that the above-mentioned liquidus surface of the ternary system was practically vertical over this temperature range, and probably up to the melting point of iron. Hence, the biliquidal (slag-metal) range should also overlap the FeO- SiO_2 join. In this connection, the point *A* was fixed by Greig by extrapolation of his actual experimental data to zero Fe_2O_3 , as his melts contained an appreciable quantity of this oxide. Above *AB* and to the right of *LA* the slag-metal liquid immiscibility becomes involved with the silicate immiscibility, and a triliquidal zone results.

Point *B* of Fig. 18(*F*) was determined by Greig from experiments carried out in air, so that the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio will be that in equilibrium with air at 1665° C. Further information on the oxygen-pressure/composition relationships in this system is provided by curves (*a*), (*b*), (*c*) and (*d*), which are derived from the work of White⁽⁸⁴⁾ and show how the state of oxidation of the iron oxide varies with the SiO_2 content in iron-oxide/ SiO_2 melts at 1619° C. and at oxygen pressures of 76, 15.2, 4 and 1 cm. of mercury, respectively. In deriving these curves it was necessary to extrapolate the original experimental data to some extent, as indicated by the broken portions of the curves. This was done on the basis of the mass-action constants deduced in the original paper. There is good agreement between Greig's determination of *B* and curve (*b*), allowing for the fact that the latter was determined at a lower temperature. The general similarity between these curves and curve *LA* is also noticeable. They are all, in fact, of the same nature, for *LA* represents conditions under an oxygen pressure in

equilibrium with metallic iron, and, though it was not determined as an isotherm, the effects of the temperature variations along it do not appear to have been very great. The tendency of the curves to converge with increasing SiO_2 content is noteworthy, as it signifies a decreasing sensitivity to the atmosphere with increasing acidity.

Incidentally, the oxygen-pressure/composition relationship revealed by these curves is more readily reconciled with the phase distribution shown in Fig. 18(*F*) than with that in Fig. 18(*E*). Curve (*b*), the air isotherm, for instance, crosses a region of the diagram in which the freezing temperatures are apparently too high for the separation of Fe_2O_3 in air, 1388°C . being, as already indicated, the maximum possible temperature at which this can occur.

Determinations of the equilibrium between the oxides of iron and the atmosphere in melts containing SiO_2 have also been made by Krings and Schackmann⁽¹¹⁰⁾ and by Salmang and Kaltenbach.⁽¹⁰⁹⁾

The effect of Al_2O_3 on the silicate immiscibility of the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ is shown in Fig. 18(*G*) by curves (1), (2), (3), (4), (5) and (6), which are due to Greig⁽⁵⁾ and show the limits of the biliquid zone in the presence of 1%, 2%, 3%, 4%, 5% and 6% of this oxide. (They are actually projections through the Al_2O_3 apex of the tetrahedron of the quaternary system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ of the intersections of the curved surface bounding the biliquid zone with the planes of these various Al_2O_3 contents.) The action of Al_2O_3 in promoting miscibility is clearly shown, though it will be noted that its effectiveness in this respect decreases as the Fe_2O_3 content increases.

(b) *The System Ca-Fe-O.*

Fig. 19(*A*) shows the phase relationships in the (solid) system Ca-Fe-O as given by Kanz, Scheil and Schulz⁽¹¹⁸⁾ on the basis of Schenck's data⁽³⁹⁾ and to account for their own observations on CaO/iron-oxide melts. The latter, however, were confined to the fields $\text{FeO}-2\text{CaO.Fe}_2\text{O}_3-\text{Fe}$ and $\text{Fe}-2\text{CaO.Fe}_2\text{O}_3-\text{CaO}$ and throw no light on other parts of the diagram. Actually, Schenck found it necessary to assume the existence of the compound $\text{CaO.Fe}_3\text{O}_4$ and another phase of unknown composition to account for certain features of his reduction curves, which were obtained at 900°C . $\text{CaO.Fe}_3\text{O}_4$ lies on the join $\text{CaO.Fe}_2\text{O}_3-\text{FeO}$ and its inclusion would necessitate the insertion of additional ties between it and the phases $2\text{CaO.Fe}_2\text{O}_3$ and Fe_3O_4 . In a later paper on this system by Schenck, Laymann and Jenckel⁽¹¹⁷⁾ a further series of reduction curves is given, and a phase diagram, based on them and on the earlier series, is reproduced. This diagram shows ties running from $\text{CaO.Fe}_3\text{O}_4$ to Fe_2O_3 (replacing that between $\text{CaO.Fe}_2\text{O}_3$ and Fe_3O_4), to Fe_3O_4 , to $\text{CaO.Fe}_2\text{O}_3$, to $2\text{CaO.Fe}_2\text{O}_3$, to the oxygen-rich limit of the wüstite range and to a point *X* of weight composition $5\text{FeO} : 2\text{Fe}_2\text{O}_3 : 2\text{CaO}$. From $2\text{CaO.Fe}_2\text{O}_3$ ties run to metallic iron, to *X*, to a point *Y* of weight composition $32.5\text{FeO} : 4.37(2\text{CaO.Fe}_2\text{O}_3)$

and to a point Z of weight composition 2.02CaO : 97.98FeO. The latter is apparently a solid solution of CaO in FeO and has a negligible Fe_2O_3 content. X and Y may also be solid solutions in wüstite, but this is not certain. Nor is it certain that they will occur in slags freezing from the liquid state, as the possibility that they may

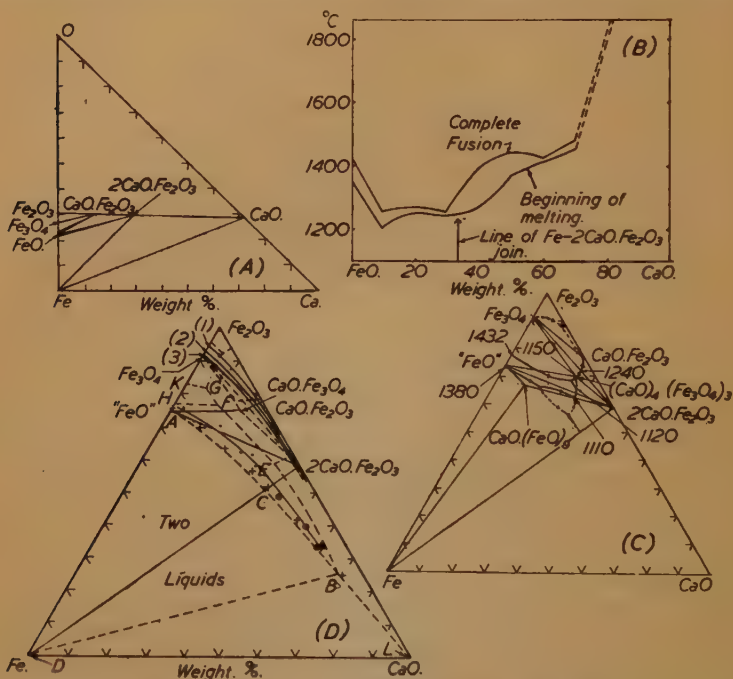
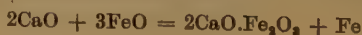


FIG. 19.—(A) Phase Relationships in the System Ca-Fe-O (Kanz, Scheil and Schulz ⁽¹¹⁸⁾). (B) Fusibility Curves of CaO-FeO Mixtures in Nitrogen (Hay and White ⁽¹²²⁾). (C) Diagram of Martin and Vogel ⁽¹²³⁾. (D) Liquidus Surface (tentative) and Oxygen-Pressure/Composition Relationships at 1592° C. of the System CaO-Fe-Fe₂O₃. Dots denote compositions of Crook's slags, ringed points those in which free CaO occurred; additional points (+) from data of Körber and Oelsen ⁽¹⁷⁸⁾ (see Section VI.(b), Addendum).

represent metastable states cannot be overlooked—not, at least, until confirmation of their existence by other methods is obtained.

From the foregoing it will be noticed that in the solid state $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is apparently stable in contact with metallic iron, and on reduction should yield iron and CaO directly. This is consistent with the fact that, as shown by Schenck's curves, it has a lower dissociation pressure than FeO at 900° C. The reaction :



between the solid phases should proceed irreversibly to the right at these temperatures, and presumably at all temperatures up to the melting point, since the samples of Kanz, Scheil and Schulz were frozen from the liquid state. The section CaO-FeO of the system Ca-Fe-O is thus not a binary one, and mixtures of FeO and CaO which lie to the FeO side of the join $\text{Fe-2CaO.Fe}_2\text{O}_3$ should, when cooled slowly from the liquid state, consist of the three phases Fe , FeO and $2\text{CaO.Fe}_2\text{O}_3$, while mixtures to the CaO side of this join should consist of Fe , $2\text{CaO.Fe}_2\text{O}_3$ and CaO . The separation of metallic iron from melts of ferrous oxide and CaO was actually described by Kanz, Scheil and Schulz, but their evidence is, perhaps, not altogether conclusive, since they used iron crucibles and "ferrous oxide" containing only 13% of oxygen. Free lime was observed only in compositions to the right of the join $\text{Fe-2CaO.Fe}_2\text{O}_3$. Hay and White⁽¹²²⁾ have reported similar results using FeO approximating to wüstite in composition. To avoid changes in composition due to contact with the crucible materials, they heated their samples in the form of pellets on platinum foil in oxygen-free nitrogen and stopped the heating as soon as the collapse of the pellet showed that fusion had occurred. A certain amount of alloying between the platinum and the iron liberated from the melts was observed, Fig. 19(B) shows the variation in the temperature of collapse of their pellets with composition. Those authors also reported confirmation of the non-occurrence of the join CaO-FeO in a later paper,⁽⁴⁶⁾ in which it was stated that the oxides CaO , MgO and FeO do not form a ternary section of the quaternary system $\text{CaO-MgO-Fe-Fe}_2\text{O}_3$; instead the composition plane $\text{CaO-Fe-2CaO.Fe}_2\text{O}_3$ occurs (see Fig. 20(F)).

An attempt to elucidate thermal as well as phase relations in part of the system Ca-Fe-O (*viz.*, in the system $2\text{CaO.Fe}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$) was made by Martin and Vogel.⁽¹²³⁾ Their diagram, which assumes their own form of the Fe-O diagram,⁽⁸²⁾ is shown in Fig. 19(C). They postulate the existence of the compounds $(\text{FeO})_9.\text{CaO}$ and $(\text{CaO})_4(\text{Fe}_3\text{O}_4)_3$; the latter lies sufficiently close to the composition $\text{CaO.Fe}_3\text{O}_4$ indicated by Schenck's results to suggest that they may be identical, but the phase distribution in its vicinity differs somewhat from that indicated by Schenck's data, as the tie $2\text{CaO.Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ is shown to occur. (They suggest that Schenck's curves may not represent true equilibrium states.) The former compound may correspond to Schenck's solid-solution phase Z. Schenck, Laymann and Jenckel⁽¹¹⁷⁾ suggest that its higher CaO content may be due to the fact that it was formed at a higher temperature than their own phase Z. Incidentally, the data of the latter workers show that the solid solution of CaO in FeO has a slightly lower dissociation pressure than pure wüstite. There may also be some small solid solubility of FeO in CaO .

It is hardly possible as yet to discriminate between the alternative phase distributions thus proposed, but in dealing with slags which

have solidified from the liquid state one would, perhaps, be biased in favour of Martin and Vogel's proposals—at least until further data become available. Further, expression of the free-energy relationships in terms of the relative dissociation pressures of the various phases as indicated by Schenck's data (assuming the identity of $(\text{CaO})_4 \cdot (\text{Fe}_3\text{O}_4)_3$ with $\text{CaO} \cdot \text{Fe}_3\text{O}_4$ and of $(\text{FeO})_9 \cdot \text{CaO}$ with the $\text{FeO}-\text{CaO}$ solid solution, and neglecting for the present the phases X and Y proposed by Schenck) leads to the conclusion that the phase distribution shown by Martin and Vogel is the most stable one.

In contrast to the above workers, Crook, who studied the constitution of $\text{CaO}/\text{iron-oxide}$ slags after melting at approximately 1450°C . in iron crucibles, is apparently of the opinion that CaO and FeO are stable in contact with each other.⁽¹²⁴⁾ He claims to have identified the compound $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ in his melts and explains the non-appearance of free lime up to and including a CaO content of 26.83% by postulating the existence of a binary join between FeO and $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$. Only on the CaO side of this join would free lime be expected to occur. Hay and White,⁽¹²²⁾ however, in discussing his results, showed that his observations with regard to the appearance of free lime are equally well accounted for on the basis of the relationships shown in Fig. 19(A), as the first of his melts to contain free lime is also the first one to the right of the tie $\text{Fe}-2\text{CaO} \cdot \text{Fe}_2\text{O}_3$. Further, they showed that the variation in the metallic-iron content of his melts is better explained by Fig. 19(A) than by the diagram proposed by him (*see below*). They also pointed out that it was by no means certain that his claim to have identified $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ in his micrographs as distinct from $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ was justified.

As described later, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ develops a considerable oxygen pressure on melting, and even when melted in platinum under an atmosphere of oxygen appreciable dissociation of the Fe_2O_3 occurs with consequent formation of ferrous oxide in the melt. Hence, it is obvious that liquid $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ cannot be completely stable in contact with metallic iron and that the relationships discussed above can only hold when the system is completely solid. Above the melting point of the slag, reduction of the Fe_2O_3 by iron with formation of FeO will occur till the composition of the liquid slag is such that it can co-exist in equilibrium with the metal. In this connection the author has observed that $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, heated in a neutral atmosphere in iron, begins to melt at just over 1200°C ., this presumably indicating the minimum temperature of formation of liquid in equilibrium with the iron. This behaviour of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ indicates the existence of a low-melting-point trough, cutting the $\text{Fe}-2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ join, in the liquidus surface of the system $\text{CaO}-\text{Fe}-\text{Fe}_2\text{O}_3$. Further information concerning this trough is obtained from a consideration of the work of Hay and White⁽¹²²⁾ and of Crook mentioned above. Thus, when the compositions of Crook's melts, suitably recalculated (*see Table I.*), are plotted within the composition triangle of the system $\text{CaO}-\text{Fe}-\text{Fe}_2\text{O}_3$, they tend to lie

on a fairly regular curve, as shown in Fig. 19(*D*) (compositions containing free CaO are ringed). Now, these melts were made in iron crucibles in a gas-fired furnace, the atmosphere of which was oxidising. The proportion of FeO to Fe₂O₃ in the various melts would, therefore, be conditioned by (1) the tendency of the melts to reach equilibrium with the iron of the crucibles, and (2) the tendency of the melts to undergo oxidation by the atmosphere. From a consideration of his results, the latter effect was probably small compared with the former (possibly because his crucibles were deep and rather narrow), and this is confirmed by the fact that his figures for the Fe₂O₃ contents of a series of iron-oxide/SiO₂ melts⁽¹²⁴⁾ prepared in iron crucibles under the same conditions agree reasonably well with those of Bowen and Schairer shown in Fig. 18(*F*), which,

TABLE I.—*Crook's Data on CaO/Iron-Oxide Melts.*

Slag No.	Chemical Analysis. %.						Composition Recalculated to CaO-Fe-Fe ₂ O ₃ . %.		
	SiO ₂ .	FeO.	Fe ₂ O ₃ .	CaO.	Metallic Iron.	MgO.	CaO.	Fe.	Fe ₂ O ₃ .
150	0.07	77.14	19.50	1.96	0.36	...	2.0	20.6	77.4
151	0.18	76.00	14.52	7.98	0.33	...	8.1	20.3	71.6
152	0.20	73.09	14.52	10.37	0.51	...	10.6	19.8	69.6
153	0.30	56.76	26.44	14.27	0.25	0.32	14.6	15.3	70.1
154	0.48	43.12	29.33	23.81	1.62	0.63	24.3	13.1	62.6
155	0.49	39.34	27.73	27.63	2.93	0.09	28.3	13.5	58.2
156	0.35	41.96	27.10	26.83	2.05	Trace	27.4	13.2	59.4
157*	0.74	34.15	24.79	38.60	0.73	...	39.3	9.7	51.0
158*	0.64	24.24	23.02	50.28	0.36	...	51.5	6.8	41.7
159*	0.92	24.34	14.24	58.25	0.22	1.16	60.0	6.8	33.2

* Melts 157, 158 and 159 contained free CaO.

as described above, were determined after melting in iron in the complete absence of oxygen, followed by quenching from the (slag) liquidus temperatures. Hence, it seems likely that Crook's melts at 1450° C. would be sensibly in equilibrium with metallic iron, *i.e.*, their compositions would be such that they would lie on the liquidus surface of the ternary system at this temperature. A little consideration will show that the part of the liquidus surface concerned will slope upwards from the above-mentioned trough to the limit of the biliquidal zone corresponding to the immiscibility between liquid slag and metal. In Fig. 19(*D*) *BEFG* represents the trough, on which the quintuple points *E*, *F* and *G* are to be expected from a consideration of the binary systems forming the sides of the ternary diagram. *E* is the intersection with the 2CaO.Fe₂O₃ peritectic line, and *F* that with the wüstite peritectic line (Fig. 15(*A*)) is assumed to be correct), while *G* is presumably a ternary eutectic of uncertain location resulting from the intersection of the trough with the FeO-Fe₃O₄ eutectic trough. On theoretical grounds it is also necessary to assume that trough *BG* will intersect the biliquidal zone

the limit of which is indicated by the line *ACBL*. The liquidus surface underlying the biliquidal zone is thus divided into two parts which dip towards and intersect along *BD* (cf. Fig. 18(*F*)). The temperature of *B*, however, is probably not much below 1519° C., the temperature of *A*. On cooling from 1450° C. Crook's melts would deposit only iron till the line *BEFH* was reached, when the slag proper would begin to freeze. If no oxygen was picked up from the atmosphere during cooling, the analysis of the melts, provided that the free-iron contents were included in their computation, would correspond to the location of the liquidus surface at 1450° C. Any oxygen pick-up would have the effect of shifting the composition down the liquidus slope nearer to the trough. In view of what has been said above, it does not seem likely that much oxygen pick-up would occur. For one thing, adjustment of the liquid composition by precipitation of iron would probably be a more rapid process than oxidation by the atmosphere to preserve the equilibrium between metallic iron and the liquid phase during the cooling. *Once freezing of the slag proper had begun, atmospheric oxidation would be an even slower process. Hence, in constructing Fig. 19(*D*), *BEFH* has been located in a manner consistent with the hypothesis that the mean curve through Crook's compositions lies on the liquidus slope at approximately 1450° C.

Freezing of the slag proper on reaching *BEFH* would be accompanied by a final adjustment towards the stable phase distribution for the solid slag. Thus, all slags lying below the join $\text{FeO}-2\text{CaO}.\text{Fe}_2\text{O}_3$ would precipitate more iron, with the formation of a corresponding amount of $2\text{CaO}.\text{Fe}_2\text{O}_3$, during the final freezing, while slags lying above this join would tend to redissolve iron precipitated during the earlier part of the cooling, with formation of FeO . Examination of Crook's data indicates that these reactions were far from complete, possibly owing to too quick cooling. Thus, he reports some metallic iron in melts lying above the $\text{FeO}-2\text{CaO}.\text{Fe}_2\text{O}_3$ join, and considerable FeO^* in slags lying in the field $\text{Fe}-2\text{CaO}.\text{Fe}_2\text{O}_3-\text{CaO}$. An indication that the last-mentioned reactions did tend to occur, however, is given by the way in which the actual metallic-iron content of his melts varies with composition; melts lying above the join $\text{FeO}-2\text{CaO}.\text{Fe}_2\text{O}_3$ are noticeably low in metallic iron, but on crossing the join there is an immediate rise in this constituent. In all Crook's slags, however, the amounts of metallic iron are too low to make much difference to the plotted points, whether they are included in the analyses or not, a fact which testifies to the incompleteness of the final readjustment on freezing and also, in all probability, to the steepness of this part of the liquidus surface.

From Fig. 19(*B*) it should be possible to fix, approximately, the melting temperatures along *BEFH*, for, as a little consideration will

* See, however, remarks on "fictitious" FeO contents due to metallic iron in Section IX.(*A*), comment No. 3.

show, melting of CaO-FeO mixtures will commence along this line, metallic iron being rejected to give the necessary shift in the composition of the liquid formed. If the upper curve of Fig. 19(B) could be considered as truly representing the completion of melting of the slag portion of the melts (as apart from the separated iron) then it would be correct to consider it as a projection of $BEFH$ through the iron corner of the diagram on a vertical plane through the compositions FeO and CaO . Actually, the determination of both curves was somewhat arbitrary, being based simply on visual inspection of the behaviour of pellets during heating, so that they cannot be considered as indicating true thermal-equilibrium relationships. (This is at once obvious in the case of the lower curve, which should have horizontal sections corresponding to the invariance of the quintuple points.) Nevertheless, the general trend of the curves shown is significant in the light of the relationships indicated in Fig. 19(D). Thus, the drop in the fusion temperature occurring up to 10% of CaO may be taken to correspond with the drop in temperature along HF , the temperature of F being apparently about 1200°C . (F may actually occur at a somewhat lower CaO content, since no determinations were made with less than 10% of CaO .) At about 30% of CaO , *i.e.*, somewhat to the left of the $\text{Fe-2CaO.Fe}_2\text{O}_3$ join in the diagram, there is a marked change in slope, which may indicate approximately the position of E , the temperature of which will then be about 1240°C . Finally, at 70% of CaO , or possibly somewhat higher—for no melts above this CaO content were actually fused, though the maximum temperature reached was 1600°C .—there is a sudden increase in the fusion temperature, which may indicate that B lies at approximately this CaO content. The fusion temperature indicated is only about 1480°C ., but it is understandable that it should be somewhat low in view of the long fusion range which a melt of this composition would have (from about 1240°C ., the temperature of E). No direct experimental evidence as to the course of the line $ACBL$ (the limit of the biliquidal zone) is available, but in view of the effect of SiO_2 on the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in equilibrium with metallic iron and of the effects of CaO and SiO_2 on the slag/gaseous-oxygen equilibrium, it is to be expected that it must be drawn in such a way that the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ will increase progressively between A and B , this tendency being further accentuated by any fall in temperature that occurs between these two points.* From B to L the relationship to be expected is not so clear, as the effect of the increasing CaO content will be counteracted by the very considerable temperature rise that must occur. L , however, must lie on the Fe-CaO side of the composition triangle, presumably close to CaO . It is to be noted that Crook's results, if it is accepted that they correspond to equilibrium with metallic iron at 1450°C ., ought to, and, in the main, do,

* On condition that no appreciable change in the activity of the metallic iron takes place with change of the CaO concentration of the slag.

show a tendency for the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio to increase with increasing CaO content. (See Addendum on next page.)

Some support for these conclusions as to the effects of CaO on the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in equilibrium with metallic iron is provided by the investigations of Krings and Schackmann⁽¹²⁵⁾ on slag-metal equilibria. Those investigators found that the addition of CaO to liquid FeO-MnO slags in contact with molten iron at 1550°C . shifted the manganese equilibrium in a way suggesting that the CaO was producing an appreciable drop in the concentration of free, as distinct from the total, FeO in the slag. This, they surmised, might be due to the formation of calcium ferrites or analogous compounds in the slag. Herty and his co-workers,⁽⁹³⁾ on the other hand, found that the addition of CaO to ferrous-oxide slags in contact with molten iron at temperatures up to 1650°C . made no difference to the partition coefficient of the FeO between the slag and metal, provided that the constant was calculated on the assumption that all of the iron oxide of the slag was reduced to the ferrous condition by the metal at high temperatures. Hence, the CaO was to be regarded as an inert diluent of the FeO . Sauerwald and Hummisch⁽¹²⁶⁾ and Körber⁽⁹⁵⁾ apparently reached a similar conclusion. On cooling to room temperature, however, Herty found, in some of his experiments, that as much as 50% of the slag iron oxide was in the form of Fe_2O_3 , mainly combined as calcium ferrites. Further, Herty elsewhere⁽¹²⁷⁾ rejects his own conclusions on this point, since, in discussing the constitution of molten basic slag, he assumes that part of the iron oxide of the liquid slag is combined as calcium ferrite. In assessing these conflicting observations it may be pointed out that the effect of CaO on the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio may be expected to decrease with rising temperature, and that the partition-coefficient experiments were, for the most part, carried out at higher temperatures than were used in obtaining the other data to which reference has been made. Nevertheless, CaO is known to have a pronounced effect on the Fe_2O_3 content of liquid slags in equilibrium with gaseous oxygen at as high a temperature as 1650°C ., so that this cannot be the full explanation. Probably the partition-coefficient determinations made hitherto have been too "rough" to show this action of the CaO . In selecting values for the partition coefficient from the experimental data available, however, preference should probably be given to determinations made with simple FeO or FeO-MnO slags.

It will be noticed that Martin and Vogel's diagram indicates a trough in approximately the same position as that shown in Fig. 19(D), though the minimum in it is placed at a considerably higher CaO content than in the latter diagram.

Curves (1), (2) and (3) of Fig. 19(D) show the effect of CaO on the composition of liquid melts of iron oxide at 1592°C . and oxygen pressures of 76, 15.2 and 4 cm. of mercury, respectively, according to the data of White.⁽⁸⁴⁾ Determinations have also been made by Salmang and Kaltenbach⁽¹⁰⁹⁾ and by Krings and Schackmann.⁽¹¹⁰⁾

Addendum.—Since the above was written a paper by Körber and Oelsen⁽¹⁷⁸⁾ has become available. Those authors give figures for the Fe_2O_3 contents of a series of CaO/iron-oxide slags which were melted (some with CaF_2 additions) at 1400–1450° C. in iron crucibles and cooled rapidly by pouring into copper chills before analysis. Compositions recalculated from their data have been plotted as crosses in Fig. 19(D) to amplify the data given there. They fall roughly parallel to Crook's compositions with, on the whole, somewhat lower Fe_2O_3 contents. Crook's melts were, of course, cooled slowly in the furnace, so some oxygen pick-up may have occurred, or else some of the iron separating during the early part of the freezing may have dropped to the bottom of the crucibles and thus escaped analysis. Körber and Oelsen point out that the Fe_2O_3 contents reported by them are likely to be somewhat too high when applied to the liquid slag and too low when applied to the solid slag. The reason is as follows: Metallic iron separating during the freezing would be represented by their analysis as FeO, while, in addition, during solution in acid it would act as a reducing agent for ferric iron, owing to hydrogen evolution. Hence, the Fe_2O_3 content would appear lower and the FeO content higher than actually occurred in the solid slag. In the limit, with complete utilisation of the evolved hydrogen in reduction, the reported analysis would be that of the liquid slag. On the other hand, if all of the hydrogen were not thus effective the reported Fe_2O_3 would be higher and the reported FeO lower than existed in the liquid slag. Körber and Oelsen's data suggest that their analyses approached fairly closely to those of the liquid slags, for, on determining the specific magnetisation of their samples, they found that, in a melt containing originally 2 mols of CaO to 3 of FeO, the specific magnetisation pointed to a metallic-iron content of about 10%. Actually, according to the equation in Section VI.(b), the metallic-iron content should have reached a maximum value at this composition, which they actually found, and its value should then have been 17.1%. The discrepancy between these figures was largely made up, however, when it was assumed that the Fe_2O_3 content reported in the analysis of this melt was that of the liquid slag prior to freezing.

It may be noted that Crook's analyses, though he determined metallic iron separately, would also be liable to deviate from those of the liquid slags, owing to hydrogen loss in dissolving. The question of the separation of iron from basic-furnace slags, and its probable effect on the analyses of the solid slag is also discussed later in the present paper (*see* Section IX.(A), comment No. 3).

(c) *The System Fe-Mn-O.*

The probable phase distribution within this system is shown in Fig. 20(A). It is based largely on a consideration of Schenck's reduction curves,⁽³⁹⁾ but is also consistent with the known characteristics of the compounds occurring. Thus, two solid-solution series

are indicated, *viz.*, that between the oxides FeO and MnO, and that between the spinels Fe_3O_4 and $\text{MnO.Fe}_2\text{O}_3$. Schenck's data are not sufficiently complete to show whether solubility is complete or not in either case. Evidence for and against complete solubility in the series FeO-MnO has already been discussed, however. The diagram as it stands is incomplete, as the phase fields of the higher oxides of manganese are not included. Actually, extension of the Fe_3O_4 - $\text{MnO.Fe}_2\text{O}_3$ solid-solution series towards the composition of Mn_3O_4 is possible, as is the formation of solid solutions between Fe_2O_3 and Mn_2O_3 . Hence, it cannot be assumed *a priori* that the join MnO-MnO.Fe₂O₃-Fe₂O₃ has any real existence (*i.e.*, that it links up conjugate compositions), and Schenck's data are inconclusive on this point.

(d) *The System Fe-Mg-O.*

The phase distribution in this system is illustrated in Fig. 20(B), which shows complete solid solubility between FeO and MgO and between Fe_3O_4 and $\text{MgO.Fe}_2\text{O}_3$. This is consistent with the form of the reduction curves of the two mixtures studied by Schenck and Dingmann,⁽⁸⁸⁾ though more definite proof of the existence of the first-mentioned series was obtained by Bowen and Schairer,⁽²⁷⁾ and of the second by Roberts and Merwin.⁽⁴⁵⁾ The work of the latter authors on the system MgO-Fe₂O₃ (*see* Fig. 9(B)) is, on the whole, consistent with the relationships shown, though they also found evidence of extensive solid solubility of MgO.Fe₂O₃ in MgO at higher temperatures.

Comparison of Figs. 20(A) and 20(B) with Fig. 19(A) shows that the action of CaO on the oxides of iron is very different from that of MnO and MgO. This may be attributed to the facts that the calcium ferrites differ in structure from the spinel group of minerals, and, therefore, do not form solid solutions with Fe_3O_4 as do MnO.Fe₂O₃ and MgO.Fe₂O₃, and also that CaO in $2\text{CaO.Fe}_2\text{O}_3$ has a much stronger stabilising action on Fe₂O₃ than have MnO and MgO in MnO.Fe₂O₃ and MgO.Fe₂O₃, so that $2\text{CaO.Fe}_2\text{O}_3$ is stable in contact with metallic iron, while MnO.Fe₂O₃ and MgO.Fe₂O₃ are not.

Information concerning the relationships within the system at measurable oxygen pressures is afforded by the work of Roberts and Merwin.⁽⁴⁵⁾ Fig. 20(C) shows the formation of FeO due to dissociation in four different mixtures of MgO and Fe₂O₃ heated under equilibrium conditions in air; the curves have been recalculated from the original data of those authors to show mols of FeO formed in the amount of the sample containing originally 1 mol of Fe₂O₃. On the same diagram a similar curve for pure Fe₂O₃ obtained by the author⁽⁸⁴⁾ is drawn for comparison. It is of interest to consider these curves in the light of the relationships given in Fig. 19(B), though strictly the latter refers to temperatures below 1000° C. All of the mixtures with the exception of (a), which corresponds to the composition MgO.Fe₂O₃, would consist initially of MgO.Fe₂O₃

and free Fe_2O_3 . On dissociation such mixtures would yield $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ – Fe_3O_4 solid solutions, since, in effect, the Fe_3O_4 formed by dissociation of the free Fe_2O_3 would dissolve in the $\text{MgO} \cdot \text{Fe}_2\text{O}_3$. In the case of pure Fe_2O_3 , the change-over from the Fe_2O_3 phase to the Fe_3O_4 phase takes place at constant temperature when the oxygen pressure is kept constant, as shown by the vertical portion of

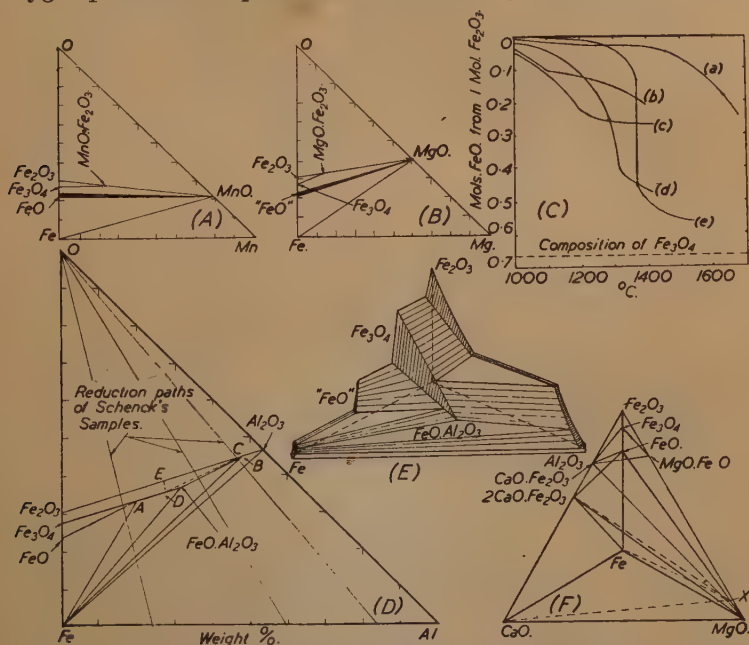


FIG. 20.—(A) Phase Relationships in the System Fe-Mn-O (mainly from Schenck, Franz and Willeke⁽³⁹⁾). (B) Phase Relationships in the System Fe-Mg-O (Schenck and Dingmann,⁽⁸⁸⁾ Roberts and Merwin,⁽⁴⁵⁾ Bowen and Schairer⁽²⁷⁾). (C) Effect of MgO on the dissociation of Fe_2O_3 in Air. $\text{MgO}/\text{Fe}_2\text{O}_3$ (by weight): (a) 20/80, (b) 17.1/82.9, (c) 13.2/86.8, (d) 5.9/94.1 (Roberts and Merwin #⁽⁴⁵⁾); (e) pure Fe_2O_3 (White⁽⁸⁴⁾). (D) Phase Relationships in the System Fe-Al-O (Schenck, Franz and Willeke⁽³⁹⁾). (E) Dissociation-Pressure Surfaces of System Fe-Al-O at 900°C . (F) Phase Diagram of the System CaO-MgO-Fe- Fe_2O_3 (Hay and White⁽⁴⁶⁾).*

curve (e)—in other words, the system is monovariant. In the three-component system containing MgO the change again involves two solid phases, Fe_2O_3 containing Fe_3O_4 (and possibly some $\text{MgO} \cdot \text{Fe}_2\text{O}_3$) in solid solution and the $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ – Fe_3O_4 solid solution, and is hence divariant and no vertical portion is to be expected on any of the curves. Further, the change-over from one phase to the other occurs at a lower temperature in the presence of

* * See Addendum, p. 695 P.

MgO than in the pure oxide, so that MgO actually appears to increase the tendency of the Fe_2O_3 to dissociate. This is attributable to the fact that $\text{MgO} \cdot \text{Fe}_2\text{O}_3$, and solid solutions of $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ in Fe_3O_4 , have a higher dissociation pressure than Fe_3O_4 alone, so that the change-over from Fe_2O_3 to the Fe_3O_4 - $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ phase can take place at a lower temperature than can the change-over to Fe_3O_4 alone. Roberts and Merwin found that the change to homogeneous spinel took place at progressively lower temperatures as the content of MgO increased. At higher temperatures, however, the curves show quite clearly the stabilising effect of MgO on the Fe_2O_3 . This is, of course, due to the formation of $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ in the system. The Fe_2O_3 thus bound would otherwise have dissociated to Fe_3O_4 when the change-over occurred.

(e) *The System Fe-Al-O.*

In this system two solid-solution series are to be expected, that between Al_2O_3 and Fe_2O_3 and that between the two spinels Fe_3O_4 and $\text{FeO} \cdot \text{Al}_2\text{O}_3$. The former is probably incomplete, as previously mentioned, while the latter is quite possibly complete. The reduction of three mixtures was studied by Schenck and his co-workers,⁽³⁹⁾ and examination of their curves reveals two apparently anomalous features with regard to the relationships involving these solid solutions. On their curve for the mixture of 1.0 mol of Al_2O_3 with 1.5 mol of Fe_2O_3 , the wüstite horizontal appears at a considerably higher oxygen content than would correspond to the crossing of the wüstite- $\text{FeO} \cdot \text{Al}_2\text{O}_3$ join, while on their curve for 10 mol of Al_2O_3 with 1.0 mol of Fe_2O_3 the $\text{FeO} \cdot \text{Al}_2\text{O}_3$ horizontal begins too early to correspond to the crossing of the $\text{FeO} \cdot \text{Al}_2\text{O}_3$ - Al_2O_3 join. Consideration of the oxygen contents at which the various breaks in their curves occur leads to the phase distribution shown in Fig. 20(D), in which neither of the joins wüstite- $\text{FeO} \cdot \text{Al}_2\text{O}_3$ or $\text{FeO} \cdot \text{Al}_2\text{O}_3$ - Al_2O_3 appear. Instead, there are joins from a composition A of the Fe_3O_4 - $\text{FeO} \cdot \text{Al}_2\text{O}_3$ series to wüstite and Fe, and from a composition B of the Al_2O_3 - Fe_2O_3 series to $\text{FeO} \cdot \text{Al}_2\text{O}_3$ and Fe. At first sight this may appear to be rather surprising, but it is apparently a necessary consequence of the fact that along the spinel solid-solution series the dissociation pressure drops progressively from a value higher than that of iron-saturated wüstite to one lower than that of iron-saturated wüstite, while a similar state of affairs exists along the Fe_2O_3 - Al_2O_3 series relative to the dissociation pressure of $\text{FeO} \cdot \text{Al}_2\text{O}_3$. It is apparently impossible to construct a pressure-composition diagram for the system, while observing the condition that the dissociation pressure must never decrease along an oxidation path, in any other way. Fig. 20(E) is a sketch of the dissociation-pressure surfaces on the basis of the phase distribution indicated in Fig. 20(D). The spinel composition to which the joins from wüstite and Fe are drawn will be that at which the dissociation pressure becomes equal to that of iron-saturated

wüstite. (The occurrence of immiscibility in the spinel series would necessitate alterations to the diagram without affecting the above conclusions materially.) Similarly, the composition of the Fe_2O_3 - Al_2O_3 series conjugate with $\text{FeO}.\text{Al}_2\text{O}_3$ and Fe will have a dissociation pressure equal to that of $\text{FeO}.\text{Al}_2\text{O}_3$. The demarcation of the immiscibility range of the Fe_2O_3 - Al_2O_3 series and of the three-phase field *CDE* is tentative only, as Schenck's data are insufficient for a definite interpretation. What evidence there is is applicable only to the tentative placing of the line *CD*, no indications of the position of *DE* being obtainable, though it may be noted that its direction must be such that *D* lies to the left and *E* to the right of any oxidation path intersecting it. If the opposite were the case the above-mentioned requirement as to the pressure variation along such a path would not be complied with.

According to Salmang and Kaltenbach,⁽¹⁰⁹⁾ Al_2O_3 acts as a weak acid in iron-oxide melts, increasing the FeO content somewhat at constant oxygen pressure and temperature.

(f) *The Quaternary System CaO-MgO-Fe-Fe₂O₃.**

On the basis of their work on the systems $\text{CaO-MgO-Fe}_2\text{O}_3$ and $\text{CaO-Fe-Fe}_2\text{O}_3$ discussed earlier, together with the results of a similar investigation of the fusibilities and mineralogical constitution of a series of CaO-MgO-FeO mixtures, Hay and White⁽⁴⁶⁾ have proposed the phase diagram for the quaternary system shown in Fig. 20(*F*). It assumes complete solid solubility between Fe_3O_4 and $\text{MgO.Fe}_2\text{O}_3$ and between MgO and FeO , in accordance with the findings of Roberts and Merwin⁽⁴⁵⁾ and Bowen and Schairer,⁽²⁷⁾ respectively. A composition plane through the phases Fe, MgO and $2\text{CaO.Fe}_2\text{O}_3$ is shown, its existence being indicated by the fact that CaO-MgO-FeO melts to the CaO-rich side of it crumbled owing to slaking on standing in air, while melts on the FeO-rich side of it were stable. This provides additional evidence of the incompatibility of FeO and CaO. At the same time no attempt was made to "bracket" the position of this plane within narrow limits, so that it is possible that a certain range of MgO-FeO solid solutions low in FeO will be capable of co-existing with free CaO, in which case the composition plane will pass through some point *X* on the join MgO-FeO instead of through MgO . This would necessitate the additional joins shown by the broken lines in Fig. 20(*F*). In constructing Fig. 20(*F*) the phase distribution given by Kanz, Scheil and Schulz⁽¹¹⁸⁾ for the system $\text{CaO-Fe-Fe}_2\text{O}_3$ was assumed to be correct (Fig. 19(*A*)). Attempts to modify Fig. 20(*F*) on the basis of the phase distribution shown in Fig. 19(*D*) reveal a possible incompatibility between Figs. 9(*C*) and 19(*D*) which throws some doubt on the authenticity of the tie $\text{MgO-CaO.Fe}_2\text{O}_3$ in Fig. 9(*C*).

* See Addendum, p. 695 P.

(g) *The Quaternary System $\text{CaO-Fe-Fe}_2\text{O}_3\text{-SiO}_2$.*

Phase diagrams for this system (or rather for the partial pseudo-system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$) have been given by Crook⁽¹²⁸⁾ and by Hay and White.⁽¹²²⁾ The former worker prepared his melts in air in magnesia crucibles, so that some pick-up of MgO occurred. MgO was thus present as a substituent in such phases as the olivines and pyroxenes, and also led to the appearance of "foreign" phases such as monticellite and diopside. It was also, presumably, responsible for the appearance of akermanite, since pure ferrous akermanite is formed only from reaction in the solid state at low temperatures and would not be expected to occur as well-formed crystals in pure CaO-FeO-SiO_2 melts. The presence of MgO , however, increases its stability (*see* discussion of the system CaO-FeO-SiO_2 , Section IV.(c)). Possibly because of this complicating factor, Crook's diagram is inconsistent with much of the work on the component ternary systems which has already been reviewed.

Hay and White determined the fusion points of $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$ mixtures heated in air on platinum foil, and made a microscopic study by reflected light of the structures obtained. Their melts could, therefore, be considered to lie on an isobaric section (oxygen pressure 15.2 cm. of mercury) through the quaternary tetrahedron, the pressure being considered effective, so far as structure was concerned, at the freezing temperature of the various melts. To supplement the facts thus obtained they made use of the available data on the systems CaO-FeO-SiO_2 , $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-Fe-Fe}_2\text{O}_3$ and $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$, all of which have already been discussed in the present paper. Hay and White, however, based their conclusions regarding the phase distribution in the two last-mentioned systems on the findings of Schenck and his co-workers, as confirmed, apparently, by Kanz, Scheil and Schulz. As indicated earlier (*see* discussions of Figs. 18 and 19) the phase distributions thus indicated appear to be in error, and this necessitates some modification of the quaternary system suggested by Hay and White. Actually, insofar as replacement of the tie $\text{Fe}_2\text{O}_3\text{-2FeO.SiO}_2$ by the tie $\text{Fe}_3\text{O}_4\text{-SiO}_2$ of Fig. 18(F) is concerned, revision of their experimental data shows that such modification is entirely justified, as the frequent appearance of Fe_3O_4 in their melts is not adequately accounted for by the original diagram, which indicates that Fe_2O_3 alone should have occurred in their melts, even though the high freezing temperatures of some of these are incompatible with the separation of this oxide in air. The altered diagram is drawn in Fig. 21(A), in which SiO_2 , CaO.SiO_2 , 3CaO.SiO_2 and 2CaO.SiO_2 are shown to be stable with both Fe_3O_4 and Fe_2O_3 , while the pyroxene and olivine solid-solution series co-exist with Fe_3O_4 instead of Fe_2O_3 as indicated previously. The diagram is intended to apply to constitutional relationships which will exist just below the freezing

points of the various melts, as these would determine the structures obtained. Hence, ferrous akermanite is not included in the phases occurring, nor is the breakdown of the pyroxene series to hedenbergite indicated. As in the original diagram, a join is shown from $3\text{CaO} \cdot \text{SiO}_2$ to FeO . Actually, this seems somewhat doubtful, for, if this were so, it would mean that the addition of metallic iron

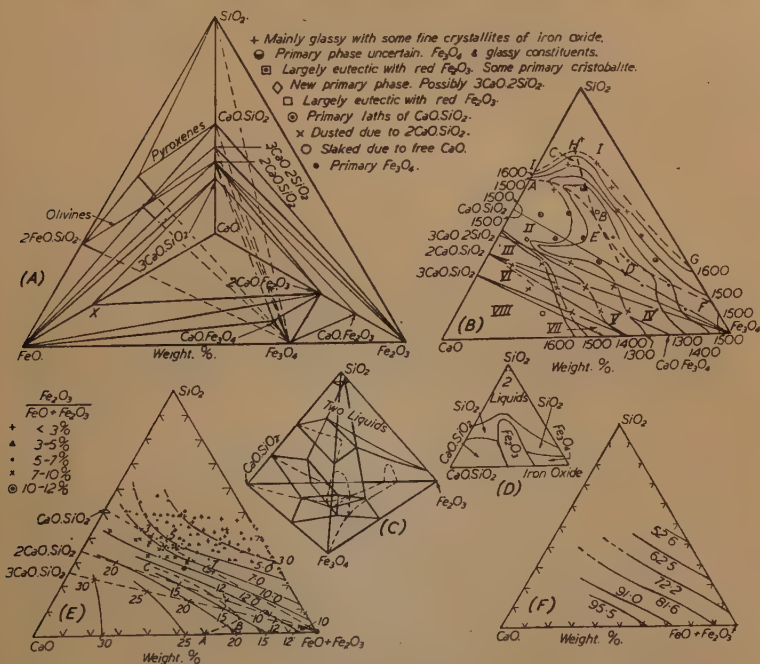
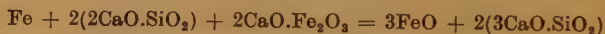


FIG. 21.—(A) Phase Distribution in the Pseudo-Quaternary System $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ (amended diagram of Hay and White⁽¹²²⁾). X is intercept of join $\text{Fe}-2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ of Fig. 19(C) on line $\text{FeO}-\text{CaO}$. (B) Fusibilities and Constituents of $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ Mixtures after Melting in Air plotted on the $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ Section of Fig. 21(A); phase fields: (I.) CaO , $\text{CaO} \cdot \text{SiO}_2$, Fe_2O_3 ; (II.) $\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot 2\text{SiO}_2$, Fe_2O_3 ; (III.) $3\text{CaO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, Fe_2O_3 ; (IV.) $2\text{CaO} \cdot \text{SiO}_2$, Fe_2O_3 , $\text{CaO} \cdot \text{Fe}_2\text{O}_3$; (V.) $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, FeO ; (VI.) $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, FeO ; (VII.) $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, FeO , Fe ; (VIII.) CaO , $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, Fe . (C) Eutectics in the System $\text{CaO} \cdot \text{SiO}_2-\text{Fe}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$. (D) Projection on a Flat Surface of Intersections of Fig. 21(C). (E) Fe_2O_3 Contents of $\text{CaO}/\text{Iron-Oxide}/\text{SiO}_2$ Melts in Equilibrium with Metallic Iron. Fe_2O_3 calculated as weight percentage of total $\text{FeO} + \text{Fe}_2\text{O}_3$ (Bowen and Schairer,⁽³⁾ Bowen, Schairer and Posnjak⁽¹²⁾; also Körber and Qelsen⁽¹⁷⁸⁾ (see Section VI.(b), Addendum)).* (F) Fe_2O_3 Contents of $\text{CaO}/\text{Iron-Oxide}/\text{SiO}_2$ Melts in Air at 1592°C. Fe_2O_3 calculated as weight percentage of total $\text{FeO} + \text{Fe}_2\text{O}_3$ (White⁽⁸⁴⁾).

* See Addendum, p. 695 p.

to compositions in the phase field $3\text{CaO}.\text{SiO}_2$ - $2\text{CaO}.\text{SiO}_2$ - FeO - $2\text{CaO}.\text{Fe}_2\text{O}_3$ in amounts sufficient to shift the composition to the free-iron side of the CaO - FeO - SiO_2 face of the diagram (*i.e.*, to a position outside the partial diagram shown, but still, of course, within the complete diagram CaO - Fe - Fe_2O_3 - SiO_2) would cause disappearance of the phase $2\text{CaO}.\text{Fe}_2\text{O}_3$. That is, reduction of the latter compound by metallic iron would have occurred in the presence of the other three phases mentioned above, in spite of the fact that all four phases are capable of co-existing singly with metallic iron. Actually, the essential point involved is whether the reaction :



will proceed to completion to the right (the behaviour indicated by the present diagram) or to the left, which would necessitate replacement of the join $3\text{CaO}.\text{SiO}_2$ - FeO by the join $2\text{CaO}.\text{SiO}_2$ - X . This, in turn, resolves itself into the question whether the increase in free energy consequent on the reduction of $2\text{CaO}.\text{Fe}_2\text{O}_3$ by iron would be less or greater than the decrease in free energy resulting from the formation of $3\text{CaO}.\text{SiO}_2$ from $2\text{CaO}.\text{SiO}_2$ and CaO .* In view of the fact that $3\text{CaO}.\text{SiO}_2$ has both an upper and a lower limit of stability,^(56, 57) the latter free-energy change is probably relatively small.

Fig. 21(B) indicates the fusibilities of the various mixtures studied by Hay and White by means of isothermal "contour" lines. The phases identified are tabulated in the diagram, and, for comparison, phase fields have been drawn in on the assumption that, owing to dissociation of the original Fe_2O_3 , the melts will lie on the section CaO - Fe_3O_4 - SiO_2 of the quaternary tetrahedron. Though this assumption is not very accurate, the agreement appears to be good. It is possible to make a somewhat closer study of relationships in that part of the system in which free SiO_2 occurs as a phase. The fusibility relationships in this part of the system, as indicated by the contour lines of Fig. 21(B), are consistent with the existence of troughs, presumably eutectics, running in the directions of the broken lines BA , BC , BD and EF (the latter not quite so well-marked as the others). This is confirmed by the fact that, on the whole, as far as can be ascertained from the data, these lines

* Körber and Oelsen⁽¹⁷⁸⁾ measured the specific magnetisation of a series of FeO - $3\text{CaO}.\text{SiO}_2$ melts which had been chilled from the liquid state. There is a maximum in their curve at about 70% of $3\text{CaO}.\text{SiO}_2$ (plus some CaF_2), which agrees well with the figure of 68% indicated by the above equation as the composition of maximum metallic-iron formation. Further, the value of the specific magnetisation at this maximum was approximately half that of a similar maximum found in their FeO - CaO series. This agrees with the fact that the theoretical iron contents to be expected at these maxima are 8.3% and 17.1%, respectively. This seems to indicate that the above equation goes to the left in the solid state, necessitating a change in Fig. 21(A) as suggested above. The presence of CaF_2 in the melts was, of course, a complicating factor.

also correspond to the boundaries of primary phase fields. Thus, primary pyroxene occurs in the field ABD - $\text{CaO} \cdot \text{SiO}_2$, and primary Fe_3O_4 in the field DEF - Fe_3O_4 . It was not always possible to decide definitely what was the primary phase in the remaining area, but a phase identified as SiO_2 was generally abundant, and in some of the melts at least skeletal crystals of cristobalite, which were probably primary, were observed. Some of these melts would not, of course, be completely fused at 1600°C ., the maximum temperature attained in these experiments, while in general the viscosity in the liquid state would be high, giving a tendency to glass formation on cooling. It was also observed that the melt, 20 CaO , 30 iron oxide, 50 SiO_2 , which lies in the immediate vicinity of point B and fused at 1280°C . was almost entirely of eutectic structure.*

The occurrence of the trough BC raises a point of some importance, in that its presence will presumably considerably affect the shape of, and probably restrict the range of, the zone of liquid immiscibility in its vicinity. No clear evidence concerning this zone was obtained from the experimental melts, but it appears that it must cover an area of approximately the shape enclosed by curve GHI in Fig. 21(B).†

To understand fully the underlying relationships between the various melts it is necessary to consider them in terms of the quaternary system $\text{CaO} \cdot \text{SiO}_2$ - Fe_3O_4 - Fe_2O_3 - SiO_2 . A qualitative sketch of the eutectic planes of this system is given in Fig. 21(C), in which the plane of the binary Fe_2O_3 - SiO_2 eutectic passes through the biliquidal zone, which occupies the high- SiO_2 region of the diagram. It may be expected that the width of the zone will be restricted appreciably where it intersects this eutectic plane. Apart from this the diagram is quite normal, with a ternary eutectic assumed to exist in each of the four ternary systems forming the faces of the tetrahedron and a quaternary eutectic located in the interior. The ternary eutectic between Fe_3O_4 , Fe_2O_3 and SiO_2 corresponds to ternary eutectic G of Fig. 18(F). Now, the structures obtained by Hay and White would be determined by the conditions attained during actual freezing, as any subsequent pick-up of oxygen that might occur during cooling in the solid state would not affect the phase distribution, though it might alter the composition of some of the phases, e.g., Fe_3O_4 might be oxidised to Fe_2O_3 during cooling without altering its crystallographic outline. (Actually, with the

* The melt 20 CaO , 20 iron oxide, 60 SiO_2 had the lowest fusion point (1260°C .) in this region.

† In placing GHI the only criterion adopted was that it should not cross the 1600°C . isotherm, as it seemed unlikely that the temperature of immiscible liquid formation would drop below this temperature. However, since the isotherms are based on the fusion points, i.e., collapse points, of the pellets, and since collapse will generally occur before complete liquefaction, the isotherms will not necessarily represent complete melting. It follows that GHI may well be too near the SiO_2 corner of the diagram, i.e., that the zone of liquid immiscibility is quite possibly more extensive than is shown.

relatively rapid cooling rates employed there was no indication of appreciable oxidation in the solid state.) Again, the particular iron oxide separating during freezing would, at constant oxygen pressure, depend solely on the temperature of freezing. Thus, iron oxide freezing out above $1388^{\circ}\text{C}.$ * (the upper limit of stability of the ferric-oxide phase in air) would do so as Fe_3O_4 , oxygen being evolved from the melt during the freezing. (This also occurs during the freezing-out of Fe_3O_4 from binary $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$ melts, as will be made clear by reference to Fig. 15(A)). Hence, melts the entire freezing range of which is above $1388^{\circ}\text{C}.$ will freeze simply as ternary mixtures of CaO.SiO_2 , Fe_3O_4 and SiO_2 , and structurally will lie on the $\text{CaO.SiO}_2\text{-Fe}_3\text{O}_4\text{-SiO}_2$ face of the quaternary diagram. The necessary condition that this should be possible is that the ternary eutectic between these three phases should be over $1388^{\circ}\text{C}.$, and the indications are that this is so. In this connection, melts need not necessarily pass through the quaternary eutectic during freezing at constant oxygen pressure, and, in fact, they will not in general do so, the reason being that at constant oxygen pressure the degrees of freedom are reduced by one, so that freezing can complete itself at a ternary eutectic. For a similar reason a binary iron-oxide melt intermediate in composition between Fe_3O_4 and Fe_2O_3 will freeze invariantly at constant oxygen pressure and without, in general, passing through the binary eutectic. Melts which freeze entirely below $1388^{\circ}\text{C}.$ —and Fig. 21(B) shows that melts in the vicinity of the central trough will do so—will pick up oxygen and separate Fe_2O_3 during freezing, and their compositions, if oxygen pick-up is complete, will lie entirely on the $\text{CaO.SiO}_2\text{-Fe}_2\text{O}_3\text{-SiO}_2$ face of the tetrahedron. Between these two extremes will lie melts which start to freeze above $1388^{\circ}\text{C}.$, separating Fe_3O_4 , and finish below this temperature, with Fe_2O_3 separating. Under equilibrium conditions the Fe_3O_4 formed in the first stage would be converted to Fe_2O_3 on passing through this temperature, but at the cooling rates employed such oxidation in the solid state would be relatively slight, and such melts would contain both Fe_2O_3 and Fe_3O_4 at room temperature. Direct evidence of the presence of Fe_2O_3 in such melts is provided by those of Hay and White, since some of the more fusible of these have a distinct reddish colour, which is visible even when viewed under the microscope by reflected light, and is then seen to be due largely to the presence of a reddish eutectic.

From the foregoing it will be seen that the "surface" (if such it can be called) on which such a series of melts will lie within the tetrahedron will be of a somewhat involved shape, since it will pass through the compositions CaO.SiO_2 , SiO_2 and Fe_3O_4 (to be exact,

* $1388 \pm 3^{\circ}\text{C}.$ is the figure given by Greig, Posnjak, Merwin and Sosman,⁽⁴⁶⁾ who determined it both for the dissociation of Fe_2O_3 to Fe_3O_4 and for the oxidation of Fe_3O_4 to Fe_2O_3 . Roberts and Merwin⁽⁴⁵⁾ give $1386 \pm 5^{\circ}\text{C}.$ The author's figure of $1368^{\circ}\text{C}.$ ⁽⁴⁴⁾ is probably less accurate. The first two temperatures are on the Geophysical Scale.

that particular composition of the Fe_3O_4 solid-solution range at equilibrium with air at its freezing point), while in the fusible region it will bulge towards the $\text{CaO}.\text{SiO}_2\text{--Fe}_2\text{O}_3\text{--SiO}_2$ face of the diagram, and over a restricted range of compositions it may actually lie wholly in that face. It is difficult to depict such a surface, but the rough form of its intersections with the various surfaces of Fig. 21(C) is indicated by broken lines drawn on these surfaces, and it will be seen that the bulge must enclose both the quaternary eutectic point and the $\text{CaO}.\text{SiO}_2\text{--Fe}_3\text{O}_4\text{--Fe}_2\text{O}_3$ ternary eutectic point. This is because the temperatures of both of these, as indicated by the low temperatures along trough BD of Fig. 21(B), must lie below 1388°C . It is also clear that the other ternary eutectics have melting temperatures above 1388°C . If, now, the intersections shown in Fig. 21(C) are considered as projected on to a flat triangular diagram, Fig. 21(D) is got, the resemblance of which to the corresponding portion of Fig. 21(B) is obvious. Trough CBD of the last-mentioned figure actually consists of two distinct troughs forming a closed loop. The curve marking the limit of the biliquidal zone has been drawn in Fig. 21(D) on the assumption that, as seems probable, the temperature of immiscible-liquid formation never drops below 1388°C . Otherwise, it would intersect this closed loop.

It is of interest to note that two of Crook's melts are described as containing Fe_2O_3 and that both of these lie close to the trough BD when their compositions are plotted on Fig. 21(B). Further, one of these, which lies close to point B in composition, appears to consist entirely of eutectic. Another point that may have some significance is that the composition of mellorite, the garnet which Hugill^(120, 129) claims to have identified in certain zones of used silica roof bricks, also falls, as regards its proportions of CaO , SiO_2 and iron oxide, in the vicinity of this trough.

Evidence regarding the equilibrium between CaO/SiO_2 /iron-oxide melts and metallic iron is provided by the work of Bowen, Schairer and Posnjak⁽¹²⁾ on the system CaO--FeO--SiO_2 . Those workers found that all of their experimental samples (though melted in iron crucibles in oxygen-free nitrogen) contained Fe_2O_3 after quenching from the liquidus temperature, *i.e.*, the temperature at which separation of solid slag, as distinct from solid metal, began on cooling. This Fe_2O_3 they determined as a percentage of the total melt in each case. If, however, the Fe_2O_3 contents of their melts are recalculated as percentages of the iron-oxide contents only, a clearer indication of the effects of the CaO and SiO_2 on the composition of the iron oxide in equilibrium with metallic iron at the liquidus temperature is obtained. It is then found that the proportion of Fe_2O_3 undergoes a systematic variation with composition as indicated in Fig. 21(E), where the variation is shown by drawing a series of lines linking up compositions having the same weight fraction of their iron-oxide content in the ferric state. In spite of the range of temperature represented, relatively few of the

actual values so obtained deviate from the distribution shown, which seems to indicate a comparatively small temperature effect up to 1500°C ., the maximum temperature reached in these investigations. The trend indicated is obvious. With increasing SiO_2 the proportion of the iron oxide in the ferric condition decreases, while with increasing CaO it increases. Hence, even when CaO and SiO_2 are present together, each acts in the same sense as when it alone is present. In effect, CaO increases the width of the biliquid range of the system Fe-O , while SiO_2 decreases it. (*See Addendum on next page.*)

The equilibrium between CaO/SiO_2 /iron-oxide melts and gaseous oxygen in the atmosphere over the melts has been studied by White⁽⁸⁴⁾ and, in less detail, by Salmang and Kaltenbach⁽¹⁰⁹⁾ and by Krings and Schackmann.⁽¹¹⁰⁾ The relationships found to hold can be expressed briefly as follows: (1) The ratio between the ferrous- and ferric-oxide contents of a given melt is determined by the temperature and oxygen pressure over the melt, increasing temperature increasing the ratio and increasing pressure decreasing it. (2) At constant temperature and oxygen pressure increasing the CaO content decreases the ratio, while increasing SiO_2 increases the ratio, these effects being found to hold when CaO and SiO_2 are present together as well as when each is present alone. Hence, CaO increases the stability of Fe_2O_3 in the melts, while SiO_2 decreases it. It follows, also, that the addition of CaO to a melt of constant ferrous- to ferric-oxide ratio decreases the dissociation pressure, while the addition of SiO_2 increases it. It is obvious that, as previously indicated, there is a close parallelism between the effects of CaO and SiO_2 on the iron-oxide/metallic-iron equilibrium and on the iron-oxide/gaseous-oxygen equilibrium. In Fig. 21(F) the variation in the percentage of Fe_2O_3 in the iron oxide in a series of CaO/SiO_2 /iron-oxide melts at 1592°C . and an oxygen pressure of 15.2 cm. of mercury according to the data of White is shown by a method of plotting similar to that used in Fig. 21(E), the weight fraction of the iron oxide present as Fe_2O_3 being constant along each of the curves shown. Actually, the melt compositions would lie on a surface passing through the quaternary tetrahedron of the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$, and the curves shown are to be regarded as projections parallel to the $\text{FeO-Fe}_2\text{O}_3$ edge of the tetrahedron on to the CaO-FeO-SiO_2 (or the $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$) face of curves of constant $(\text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3)$ ratio lying on this surface.

From the physico-chemical point of view these relationships are most readily explained by the hypothesis that the equilibrium between the oxides of iron in the melt and their surroundings (oxygen-saturated iron with the oxygen pressure in equilibrium with it in the one case, and gaseous oxygen in the other) is displaced as the result of compound formation. If it be assumed that the proportions of FeO and Fe_2O_3 in the melts are conditioned by reversible equilibria of the type:



it follows that any substance forming a stable compound with Fe_2O_3 will shift the equilibrium in such a way that the total Fe_2O_3 content of the system will be increased, while substances forming stable compounds with FeO will act in the opposite direction. The fact that CaO belongs to the first category and SiO_2 to the second can be taken to indicate that the compounds formed, *viz.*, calcium ferrites and ferrous silicate, are at least partially stable in the liquid state.

Addendum.—In the paper by Körber and Oelsen⁽¹⁷⁸⁾ to which reference has already been made earlier, the Fe_2O_3 contents of four series of melts, *viz.*, $\text{FeO}-\text{CaO}$, $\text{FeO}-3\text{CaO}.\text{SiO}_2$, $\text{FeO}-2\text{CaO}.\text{SiO}_2$, and $\text{FeO}-\text{CaO}.\text{SiO}_2$, after melting at $1400-1450^\circ\text{C}$. in soft-iron crucibles, are given. These data have been inserted in Fig. 21(E), in which the three straight broken lines represent the last three of these series, the first lying along the $\text{CaO}/\text{iron-oxide}$ edge of the diagram. Along these lines the small numbers indicate the compositions at which the expression $(100 \text{ Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3)$ reaches the values 10, 12, 15, 20, 25, 30, &c. (Along the first three series the value of the expression increases continuously as the content of CaO or calcium silicate increases, but along the last series it continuously decreases as indicated.) By joining up appropriate points, lines corresponding to the values 15, 20, 25 and 30 have been inserted. Though there is a certain degree of discrepancy where the new data overlap those from Bowen and Schairer's papers—Körber and Oelsen's Fe_2O_3 contents are seen to be somewhat low relative to Bowen and Schairer's—yet the direction of the additional curves so obtained is in good agreement with that of the earlier curves.

The broken curve *ABC* encloses on its left-hand side the compositions to which Körber and Oelsen found it necessary to add spar to achieve melting at $1400-1450^\circ\text{C}$. It can be regarded, therefore, as a rough isotherm, to the right of which lie all compositions fusible at or below $1400-1450^\circ\text{C}$. Attention is drawn to the form of this curve in connection with the statement made in comment (4) of Section X. in discussing the trend of the isotherms of the system $\text{CaO}-\text{FeO}-\text{SiO}_2$ as shown in Fig. 3(A).

VII.—GAS OXIDATION *VIA* THE SLAG IN THE OPEN-HEARTH FURNACE.

The relationships described in the preceding Sections are of fundamental importance from the point of view of the behaviour of the slag in the furnace. Thus, at its upper surface the slag is constantly tending to come to equilibrium with the oxidising atmosphere over it, which state will only be attained when the Fe_2O_3 to FeO ratio reaches a value appropriate to the oxygen pressure of the furnace atmosphere and the temperature and composition of the slag. At the slag-metal surface, on the other hand, the equilibrium state is entirely different, and corresponds to a much lower Fe_2O_3 content in the slag. The conditions at the two

slag surfaces are thus incompatible, and hence a continuous cycle of operations is set up—oxidation of FeO to Fe_2O_3 by the gases occurring at the upper surface, while, simultaneously, reduction of Fe_2O_3 to FeO by the metal proceeds continuously at the lower surface, this latter reaction being accompanied by the oxidation of metal from the bath to FeO . This FeO , if not used up immediately in refining, is then in turn available for repeated oxidation and reduction, and thus contributes to the gas-oxidation cycle. Hence, gas oxidation tends to be cumulative in its effects. In the early stages of the process these effects are masked by the rapid reduction of the iron oxides of the slag by the bath, which is then highly charged with metalloids, but towards the closing stages the rate of reduction of iron oxide decreases, and there is then an increase in both the Fe_2O_3 content and the total iron-oxide content of the slag. In the acid process this takes place to a moderate extent only, and does not interfere with control of the finishing stages, but in the basic process a marked increase in the iron oxides of the slag and of the FeO in the metal is a characteristic feature of the period following the termination of the boil. This difference between the two processes is associated with a marked difference in the ratio of Fe_2O_3 to FeO in the two types of slag, the ratio being characteristically higher in basic slags than in acid slags, a fact which is accounted for by the relationships already discussed. Thus, Whiteley⁽¹³⁰⁾ found that the proportion of the iron oxide as Fe_2O_3 was approximately 6.6% in an acid slag and 25% in a basic slag towards the end of the respective processes. He was also able to show that the Fe_2O_3 content of basic slags decreased as the sum of the P_2O_5 and SiO_2 contents increased. McCance⁽¹³¹⁾ earlier demonstrated a similar effect due to increasing SiO_2 in certain scales.

The point has sometimes been raised as to why the higher Fe_2O_3 to FeO ratio in basic slags should lead to increased gas-oxidation when the additional Fe_2O_3 in these slags is presumably largely combined as stable compounds of lime (this supposition is supported by the present author's calculations on the constitution of liquid CaO/SiO_2 /iron-oxide slags). This represents a problem in chemical kinetics which cannot be fully answered without a knowledge of the relative speeds of dissociation of the various compounds involved. Viewing the problem from a somewhat different standpoint, however, it may be pointed out that comparison of Figs. 21(E) and 21(F) indicates that there will probably be a greater difference between the slag-gas and slag-metal equilibrium states, as measured by the content of iron-combined oxygen, in basic slags than in acid slags. Thus, in basic slags the percentage of the iron oxide content as Fe_2O_3 will apparently be of the order of 80–90% when in equilibrium with air at 1592°C . and about 12% when in equilibrium with metallic iron. In acid slags the figures will be apparently about 40–50% and about 3%, respectively. (This assumes that the other basic oxides in the slag are roughly equivalent to CaO in effect, and

that the other acid oxides are roughly equivalent to SiO_2 . As might be expected, Whiteley's figures quoted above indicate an intermediate state of oxidation in each case.) As a consequence, the difference in free energy between the two equilibrium states is quite likely greater for basic slags than for acid slags. In other words, the difference in chemical potential between the two states is greater for basic than for acid slags.*

The question of gas-oxidation in the basic process has occupied the attention of many writers,^(127, 132, 133) and various methods of bringing it under control have been suggested. There are apparently three main ways in which this may be done: (1) By keeping the iron-oxide content of the slag as low as possible by direct means, e.g., by quick melting, avoidance of large amounts of light scrap, judicious feeding in the early stages, &c. (Control from the beginning of the process is necessary, since the activity of the slag as regards gas-oxidation, being the result of a recurring cycle, is hereditary, and the state of the slag at any time influences its state at all subsequent times.) (2) By judiciously controlling the silicon content of the charge, and thus the SiO_2 content of the slag, so as to diminish the action of CaO and thus decrease the Fe_2O_3 content of the slag at all stages of the process. (3) By cutting down the supply of air to the furnace to a minimum, especially towards the end of the process.

VIII.—THE MINERALOGICAL CONSTITUTION OF ACTUAL FURNACE SLAGS AND INFLUENCES AFFECTING THEIR COMPOSITION.

Acid Slags.

(a) *Constitution.*

Acid furnace slags to which little or no lime has been added may consist of up to 95% of FeO , MnO and SiO_2 , and, therefore, approximate closely to slags of the simple ternary system FeO-MnO-SiO_2 (see Fig. 2). Finishing slags of this type usually contain approximately 50–55% of SiO_2 and are thus close to saturation with that oxide at steelmaking temperatures, and hence are not far from equilibrium with the silica hearth. The mineralogical constitution of such slags has been found to agree well with the relationships shown in Fig. 2. In the slowly cooled or annealed condition they consist usually of primary SiO_2 in a ground-mass composed mainly of silicates of the fayalite-tephroite series. When sufficient MnO is present, rhodonite containing FeO in solid solution appears, replacing these silicates or, if the SiO_2 content of the slag is low enough, replacing SiO_2 as the primary phase. As previously described, Whiteley and Hallimond⁽²³⁾ found that rhodonite appeared in the slag when the ratio of MnO to FeO exceeded 27/73, the ratio in the resulting rhodonite then being 29/71.

* Viscosity differences may also play a part.

The effects of adding lime to acid slags have already been indicated (see Fig. 7(B)). Up to 7.8% the CaO enters the ordinary slag silicates as a substituent. Above this figure vogtite appears in the slag. As regards the minor constituents normally present, MgO also occurs as a substituent both in the normal silicates and in vogtite if sufficient CaO is present to give this constituent. Al_2O_3 and Fe_2O_3 , according to the relationships revealed by the relevant diagrams, will occur as mullite and Fe_3O_4 , respectively, but there does not appear to be any direct evidence of this, possibly because the amounts of these constituents will normally be small.* On the other hand, the possibility that they might occur in solid solution in the silicates cannot be entirely precluded, as small amounts of both often occur in the natural silicates.

(b) *Fusibility-Composition Relationships.*

The saturation concentration of SiO_2 in FeO-MnO-SiO_2 slags at steelmaking temperatures is approximately 50% and is little affected by variations in the FeO/MnO ratio.⁽²⁶⁾ An important effect of CaO in such slags is that it increases this value. Thus, Körber⁽⁵⁹⁾ found the following values at saturation at 1600° C. for the SiO_2 content of FeO-MnO-SiO_2 slags to which CaO had been added :

CaO.	%	Nil	12	18	34
SiO_2 .	%	48-52	57	60	63

Hay, Ferguson and White⁽¹³⁴⁾ showed, from the statistical examination of 110 acid finishing slags, that the ratio of the molecular percentage of $(\text{FeO} + \text{MnO} + \text{CaO})$ to that of SiO_2 was appreciably constant and equal to approximately 0.60-0.66. (It was actually somewhat lower for high-carbon heats than for low-carbon heats.) From the point of view of their fluxing action on the SiO_2 it would appear, therefore, that, molecule for molecule, FeO, MnO and CaO are mutually replaceable by one another in quaternary slags of this type (at least over the composition range usually encountered in practice). This result, which is probably an average one only, arises from the fact that CaO, which, weight for weight, is the most effective flux, has also the lowest molecular weight of the three

* In view of Schairer's recent work on the ternary system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ and on the quaternary system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ (see second footnote to Section IV.(h) and also Fig. 11(F)), these conclusions must now be modified somewhat. The addition of Al_2O_3 to CaO-free FeO-MnO-SiO_2 slags of high SiO_2 content should lead to the formation of spinel before mullite. This spinel will presumably contain MnO as well as FeO, and also any Fe_2O_3 which may be present. When CaO is also present, the addition of Al_2O_3 should lead to the appearance of anorthite, possibly associated with spinel if the ratio of CaO to the other bases is low, but without spinel, except possibly magnetite, if this ratio is high. In the quaternary system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$, the phase assemblages occurring in the solid slag would be tridymite-olivine-anorthite-hercynite, tridymite-wollastonite(metasilicate solid-solution series)-olivine-anorthite and tridymite-wollastonite(metasilicate solid-solution series)-anorthite.

basic oxides. An attempt to show the relationships involved somewhat more closely within the framework of the quaternary system CaO-FeO-MnO-SiO_2 is made in Fig. 22(A), weight percentages being employed. For this purpose use has been made of the slag compositions utilised by Hay, Ferguson and White,⁽¹³⁴⁾ augmented by other finishing-slag compositions taken from the

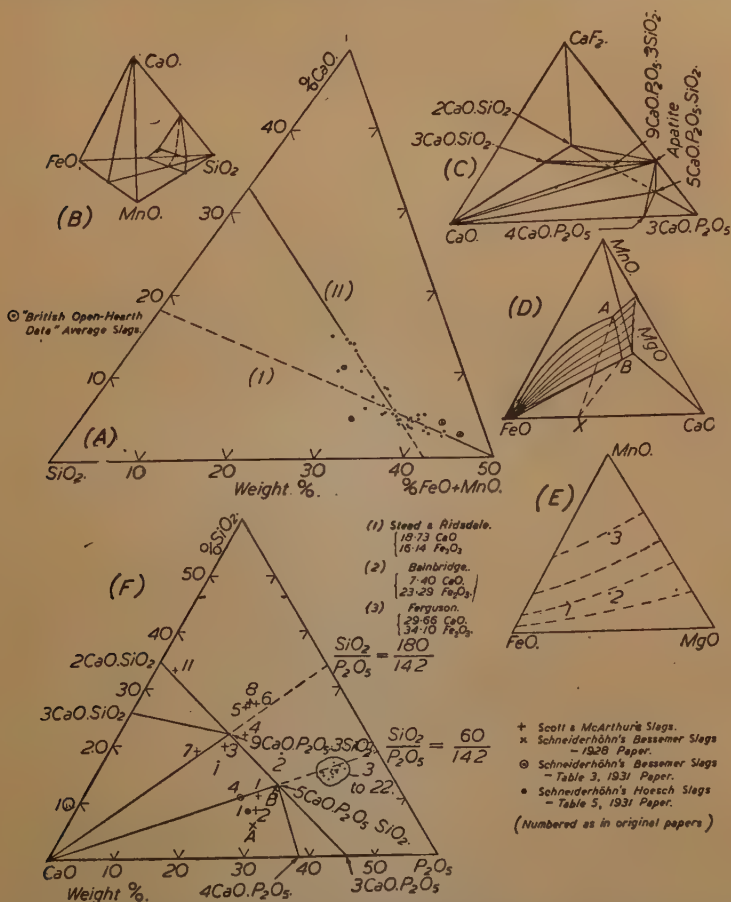


FIG. 22.—(A) Compositions of Acid Finishing Slags in Terms of their CaO-FeO-MnO-SiO_2 Contents. Compositions projected on to central section through quaternary diagram. (B) Position of Mean Planes in the Quaternary Diagram. (C) Phase Distribution in $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ Slags containing CaF_2 (not to scale). (D) Suggested Phase Relationship between the Divalent Oxides of Basic Slags. (E) Compositions of Free-Oxide Phases of Stead and Ridsdale,⁽¹⁴¹⁾ Bainbridge⁽¹⁴⁴⁾ and Ferguson.⁽¹⁴⁶⁾ (F) Influence of the $\text{SiO}_2/\text{P}_2\text{O}_5$ Ratio of Basic Slags on their Constitution (slags of Scott and McArthur,⁽¹⁴⁵⁾ Schneiderhöhn^(77, 147)).

literature. It was necessary to restrict these latter to slags from normally-run charges, for many of the published papers which give slag compositions deal with heats run with abnormal slags to provide data on slag-metal reactions. Wherever the published data were sufficiently explicit to make this possible, the compositions taken have been those of the finishing slags just prior to the finishing additions, since some change in slag composition invariably follows the making of these additions. Table II. shows the compositions of the slags taken in terms of their contents of CaO, MnO, FeO and SiO₂, recalculated to sum to 100%. To plot these compositions within a quaternary diagram as drawn on a two-dimensional surface presents obvious difficulties, so recourse was had to the device of plotting their normal projections on the plane bisecting the tetrahedron perpendicular to its FeO-MnO-SiO₂ face (*see* Fig. 22(B)), this plane being chosen because it was intended primarily to demonstrate the effect of CaO on the SiO₂ contents of the slags. When this was done it was found that considerable scattering of the plotted points occurred, though the general trend due to increasing CaO was shown clearly enough. Some scattering was, of course, to be expected, but it was noticed that there was a tendency for slags with a high ratio of MnO to FeO to have higher SiO₂ contents than those with a low value of this ratio. It appeared, therefore, that the mean plane through the slag compositions prior to projection was not normal to the bisecting plane, but that it cut the MnO-SiO₂ edge of the tetrahedron at a higher SiO₂ content than that at which it cut the FeO-SiO₂ edge. An attempt was, therefore, made to find a plane which, when the slag compositions were projected parallel to it and to the FeO-MnO-SiO₂ face of the tetrahedron, would give minimum scattering on the bisecting plane. Actually, it was found that two planes, intersecting along a line parallel to the FeO-MnO-SiO₂ face and corresponding to a constant CaO content of 5%, fitted the distribution of the slag compositions very well. The equations of these planes with respect to the inclined axes formed by the three edges of the tetrahedron passing through the SiO₂ apex are :

$$\frac{\text{FeO}}{64} + \frac{\text{MnO}}{40} + \frac{\text{CaO}}{18} = 1 \quad (1) \quad \text{and} \quad \frac{\text{FeO}}{54.3} + \frac{\text{MnO}}{34} + \frac{\text{CaO}}{33} = 1 \quad (2).$$

the former applying to CaO contents up to 5% and the latter to CaO contents over this. It is probable that too much significance should not be attached to the points of intersection between these planes and the binary edges of the tetrahedron, since these points lie well outside the range of compositions represented by the slags considered, but it is of interest that the point of intersection of plane (2) with the CaO-SiO₂ edge corresponds closely with the SiO₂ saturation value of CaO-SiO₂ slags at 1600° C. as indicated by Fig. 1(C). The position of the planes in the quaternary diagram does, in fact, suggest that they are closely related to the liquidus surface corresponding to saturation with SiO₂ at steelmaking temperatures,

TABLE II.—*Slag Compositions.*

$$\text{Equations: (1) } \frac{\text{FeO}}{64} + \frac{\text{MnO}}{40} + \frac{\text{CaO}}{18} = 1. \quad (2) \frac{\text{FeO}}{54.3} + \frac{\text{MnO}}{34} + \frac{\text{CaO}}{33} = 1.$$

Source.	Steel.		Slag.				Equation Used.	Value of Left Side of Equation.
	No.	C. %.	SiO ₂ %.	FeO %.	MnO %.	CaO %.		
Hay, Ferguson and White, ⁽¹²⁴⁾ <i>loc. cit.</i> , p. 62.	1	0.19	56.9	27.4	10.4	5.3	2	0.972
	2	0.15	56.3	21.8	17.0	4.9	1	1.038
	3	0.17	57.2	21.6	16.7	4.5	1	1.005
	4	0.17	55.6	22.3	18.3	3.8	1	1.016
	5	0.17	55.3	23.8	17.5	3.4	1	0.999
	6	0.16	54.0	26.5	16.8	2.7	1	0.984
	7	0.16	51.8	28.8	16.9	2.5	1	1.011
	8	0.25	58.9	18.1	19.6	13.4	2	1.021
	9	0.33	59.3	18.3	11.4	11.0	2	1.005
	10	0.29	58.0	21.1	11.3	9.6	2	1.012
	11	0.26	56.8	22.5	12.6	8.1	2	1.029
	12	0.25	56.4	23.3	12.7	7.6	2	1.032
	13	0.27	57.0	23.6	12.7	6.1	2	0.993
	14	0.24	57.9	21.6	15.4	5.1	2	1.004
	15	0.27	58.5	20.0	17.0	4.5	1	0.998
	16	0.26	57.4	21.4	17.4	3.8	1	0.980
	17	0.22	53.6	22.6	20.7	3.1	1	1.043
	18	0.75	60.5	15.4	9.6	14.5	2	1.007
	19	0.75	60.5	13.2	18.0	8.3	2	1.024
	20	0.42	59.4	20.6	12.6	7.4	2	0.974
	21	0.74	60.5	20.3	13.2	6.0	2	0.945
	22	0.43	58.5	19.3	16.7	5.5	2	1.013
	23	0.46	57.5	17.3	20.2	5.0	1	1.053
	24	0.47	59.3	17.5	18.7	4.5	1	0.992
	25	0.44	59.8	16.7	19.5	4.0	1	0.970
	26	0.41	59.0	17.0	20.5	3.5	1	0.972
Herty and Jacobs. ⁽¹²⁷⁾	...	0.49	57.1	16.3	21.6	5.0	1	1.073
	...	0.17	57.3	19.6	18.8	4.3	1	1.015
Bramley, Maddocks and Tateson. ⁽¹²⁸⁾	61.1	13.6	11.7	13.6	2	1.007
McCance, ⁽¹²¹⁾ <i>loc. cit.</i> , p. 268.	54.6	24.6	16.1	4.7	1	1.046
Service, ⁽¹²⁹⁾ Last samples from charges 1 to 4 before finishings added.	1	0.21	64.2	13.1	12.2	10.5	2	0.918
	2	0.67	60.1	13.8	22.2	5.9	1	0.987
	3	...	59.5	18.8	11.3	10.4	2	0.994
	4	...	63.7	12.8	8.6	14.9	2	0.940
Reinartz. ⁽¹³⁰⁾	63.8	14.2	13.4	8.6	2	0.916
Wood. ⁽¹³¹⁾	...	0.51	61.0	13.4	12.9	12.7	2	1.011
	...	0.26	57.6	23.2	13.9	5.3	2	0.981
Styri, ⁽¹³²⁾ Heat 41,246; 10.40 sample before Fe-Mn.	...	0.32	58.9	18.2	17.9	5.0	1	1.010
"British Open Hearth Data and their Correlation." ⁽¹²³⁾ Average slags.	1	...	61.3	17.8	9.9	11.0	2	0.952
	2	...	46.7	38.8	11.8	2.7	1	1.051
	5	...	52.4	25.6	17.8	4.2	1	1.078
	6	...	59.0	30.0	6.3	4.7	1	0.888

though the marked increase in the SiO₂ content when MnO is increased at the expense of FeO is rather different from what would be expected from the trend of the liquidus surface of the

system FeO-MnO-SiO_2 , if the data relating to this system are correct, for these indicate little change in the saturation concentration of SiO_2 with changes in the ratio of FeO to MnO . (This is also confirmed by the findings of Körber mentioned earlier.) Of course, high accuracy is not claimed in respect of the differentiation between the coefficients of FeO and MnO in the above equations, but, nevertheless, the difference indicated is in keeping with the reputedly greater corrosive action on silica refractories of slags high in MnO . A possible explanation is that MnO increases the fluidity of acid slags, and hence increases the content of SiO_2 that can be carried before the slag becomes unworkable. If this is so, increasing viscosity rather than actual saturation with SiO_2 may be the ultimate factor limiting the SiO_2 content of acid slags. This conception was previously discussed by Macnair.⁽¹³⁵⁾

In the last column of Table II. are shown the results obtained by evaluating the left-hand side of the appropriate equation for the various slag compositions, equation (1) being used for CaO contents up to 5% and equation (2) for higher CaO contents. Values less than unity indicate that the composition lies to the SiO_2 side of the appropriate plane, while values greater than unity that it lies to the opposite side. It is evident from the values obtained that most of the compositions lie reasonably close to the stated planes. Closer concentration of the plotted points about the planes is probably not to be expected, since, for one thing, temperatures would be liable to vary somewhat from furnace to furnace. Further, different operators would not necessarily finish with the slag in the same condition, some being likely to prefer more fluid slags than others. In this connection Ferguson⁽¹³⁶⁾ has described two distinct types of finishing slag, one viscous and inactive and the other fluid and active, each having its own particular advantage from the steel-making point of view. Hence, though for convenience the relationships under discussion have been defined in terms of mean planes passing through the slag compositions, it is probably more correct to regard the compositions as distributed within a restricted zone, the stated planes being situated at approximately the centre of this zone. The width of this zone will then correspond to the range of SiO_2 contents giving workable slags.

The change in direction at 5% of CaO shown in Fig. 22(A) appears to indicate that the fluxing action of CaO is most pronounced up to this concentration, and is possibly related to the occurrence of the immiscibility gap in the metasilicate solid-solution series between the rhodonite series and vogtite postulated in Fig. 7(B). Such a gap might possibly give rise to a eutectic trough in the liquidus of the quaternary system. It is not intended to claim finality for the above findings, however, as, for a method that is essentially statistical in its implications, the number of slag compositions available was rather low.

*Basic Slags.**(a) Constitution.*

Constitutionally, basic slags are considerably more complex than acid slags, since they normally contain significant amounts of CaO , P_2O_5 , SiO_2 , FeO , Fe_2O_3 , MnO , MgO and Al_2O_3 . Hence, their phase and thermal relationships cannot be adequately represented on a single diagram. Chemically, the outstanding feature of such slags is that the basic-oxide content is more than sufficient to neutralise the acid oxides, and, in fact, in many cases the CaO content alone is sufficient to do this. In such slags, since CaO is the strongest base present, substantially all the SiO_2 , P_2O_5 , Fe_2O_3 and Al_2O_3 will be combined with it in the solid slag. In general, only if there is a deficiency of CaO in this respect will other bases be found in combination with the acid oxides. The mineralogical constitution of basic (including Bessemer) slags has been the subject of a considerable number of investigations, notably those by Vogt,⁽¹³⁷⁾ Carnot and Richards,⁽¹³⁸⁾ Hilgenstock,⁽¹³⁹⁾ von Groddeck and Broockmann,⁽¹⁴⁰⁾ Stead and Ridsdale,⁽¹⁴¹⁾ Bücking and Linck,⁽¹⁴²⁾ Kroll,⁽¹⁴³⁾ Bainbridge,⁽¹⁴⁴⁾ Scott and McArthur,⁽¹⁴⁵⁾ Ferguson⁽¹⁴⁶⁾ and Schneiderhöhn.^(77, 147) A list of the constituents identified by these workers is given in sub-sections (b) to (f) below. For fuller details of their crystallographic and optical characteristics the original papers should be consulted.

(b) Free Lime.

Schneiderhöhn⁽⁷⁷⁾ found CaO in a fine state of dispersion in some of his slags, but it had been formed by the action of moisture on $4\text{CaO} \cdot \text{P}_2\text{O}_5$ during cooling (see discussion on the system $\text{CaO}-\text{P}_2\text{O}_5$, Section IV.(l)). No evidence of the presence of CaO as a phase which had crystallised from the liquid slag was found by any of the above-mentioned workers. Chemical analysis indicates that it is present in the free-oxide phase described, though its solubility in that phase is presumably limited. This absence of free CaO even from slags of high CaO content appears significant in view of the incompatibility of CaO and FeO indicated in Fig. 19.

(c) Calcium Silicates, Phosphates and Silico-Phosphates.

(1) *Tricalcium Silicate* ($3\text{CaO} \cdot \text{SiO}_2$).—This compound was identified by analysis and by its optical properties in an apatite-bearing slag by Ferguson.

(2) *Calcium Orthosilicate* ($2\text{CaO} \cdot \text{SiO}_2$).—Scott and McArthur identified $2\text{CaO} \cdot \text{SiO}_2$ (the γ form) by means of its optical properties in slag of high $\text{SiO}_2/\text{P}_2\text{O}_5$ ratio, and also in apatite-bearing slags. It was also found by Schneiderhöhn to be a characteristic constituent of the latter type of slag.

(3) *Hilgenstockite* ($4\text{CaO} \cdot \text{P}_2\text{O}_5$).—Separation and analysis of this compound from Bessemer slags has been carried out several times.⁽¹³⁸⁻¹⁴²⁾ It has also been identified microscopically by Schneiderhöhn in Bessemer slags.

(4) *Steadite*.—This constituent has been separated and analysed by Stead and Ridsdale and by Bucking and Linck, and has been identified microscopically by Scott and McArthur and by Schneiderhöhn. Stead and Ridsdale considered it to be $4\text{CaO} \cdot \text{P}_2\text{O}_5$ with about 10% of impurity, largely iron silicate, while Bucking and Linck wrote its formula $4(3\text{CaO} \cdot \text{P}_2\text{O}_5) \cdot 3\text{CaO} \cdot \text{SiO}_2$ and considered it to be a silico-phosphate with a structure similar to that of apatite. Expressed in terms of their CaO , P_2O_5 and SiO_2 contents, the compositions given by the above workers lie within or immediately adjacent to the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ homogeneity range indicated in Fig. 14(B). It seems reasonable to assume that it is a $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution containing, possibly, not only CaO and SiO_2 in solid solution but also small amounts of FeO , MnO and MgO .

(5) *Silico-Carnotite* ($5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$).—Separation and analysis has been effected by Carnot and Richards, Stead and Ridsdale, Bucking and Linck, and Hilgenstock, and it has been identified microscopically by Scott and McArthur and by Schneiderhöhn. Von Groddeck and Broockmann also succeeded in isolating small crystals of this constituent from slags, but, owing probably to the smallness of the amount available for analysis, failed to detect SiO_2 , and concluded that it was another form of $4\text{CaO} \cdot \text{P}_2\text{O}_5$. This was supported by Hilgenstock, who considered that the silico-phosphates were merely different forms of the latter compound with the SiO_2 present as an impurity, the particular form appearing depending on the conditions during its separation.

(6) $9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$.—This compound, which exists in the system $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ according to Körber and Trömel^(69, 70) (see Fig. 14(B)), would be expected to occur in basic slags in which the ratio of SiO_2 to P_2O_5 is greater than 60/142. It has not yet been isolated from basic slags apparently, but Scott and McArthur concluded from their own observations that a silico-phosphate with a 3/1 ratio of SiO_2 to P_2O_5 existed in those of their slags which were of this type. It seems reasonable to identify this with $9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$, for, though they indicate a somewhat lower content of CaO , their method of calculation was somewhat arbitrary.

(7) $6\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2 \cdot 2\text{FeO} \cdot \text{SiO}_2$ (*Octobasic Phosphate*).—Kroll claimed to have separated this compound from basic slags studied by him, and considered it to comprise the bulk (the "mother-mass") of all basic slags, from which other silico-phosphates could form only by decomposition during slow cooling. No other workers appear to have found this constituent, and its nature is, therefore, uncertain. The crystals of which he shows photographs were, however, hexagonal in cross-section, and the $\text{SiO}_2/\text{P}_2\text{O}_5$ ratio indicated by his analyses lies at about the limit indicated by Körber and Trömel for the

$3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid-solution range (Fig. 14(B)). It may, therefore, have been a member of the same solid-solution series as steadite, and the slag analysis which he quotes as typical of those studied by him does, in fact, indicate that his slags would consist mainly of this solid solution. With regard to his statement that decomposition of this compound during slow cooling gives rise to other silico-phosphates, it might be possible that the transformation of the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ from the α to the β form during cooling might give rise to some such effect, e.g., if the transformation were accompanied by a decrease in the solid solubility. There does not appear to be any information on this point at present, however.

(8) *Fluorapatite (or Apatite)* ($3(3\text{CaO} \cdot \text{P}_2\text{O}_5) \cdot \text{CaF}_2$).—This constituent, which has a very low citric-acid solubility, is characteristic of all slags to which fluorspar has been added.^(144-146, 77) According to Scott and McArthur, it is commonly associated with $2\text{CaO} \cdot \text{SiO}_2$, but $3\text{CaO} \cdot \text{SiO}_2$ ⁽¹⁴⁶⁾ and what was probably $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ ⁽¹⁴⁴⁾ have also been found with it, the nature of the silicate being determined probably by the amount of CaO available. If sufficient CaF_2 is present, all the P_2O_5 of the slag occurs as apatite; if not, apatite is found to co-exist with normal phosphates and silico-phosphates, e.g., steadite (Sheldon⁽¹⁴⁸⁾) or silico-carnotite (Schneiderhöhn⁽⁷⁷⁾). The reaction involved was demonstrated by Bainbridge, who showed that the addition of CaF_2 to synthetic $4\text{CaO} \cdot \text{P}_2\text{O}_5$ and $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ liberated CaO and $2\text{CaO} \cdot \text{SiO}_2$, respectively, while the citric-acid solubility dropped progressively with increasing CaF_2 content, reaching a minimum, and, thereafter, constant value at a $\text{CaF}_2/3\text{CaO} \cdot \text{P}_2\text{O}_5$ ratio of approximately 8/100. (In pure apatite the ratio is 94/1042.) He found similar relationships for the case of CaF_2 additions to a citric-acid-soluble slag of known phosphorus content. A tentative phase diagram for the system $\text{CaO}-3\text{CaO} \cdot \text{P}_2\text{O}_5-2\text{CaO} \cdot \text{SiO}_2-\text{CaF}_2$ based on the above observations is shown in Fig. 22(C).

(d) *Substituted Silicates and Silico-Phosphates.*

Silicates and silico-phosphates in which part of the CaO is replaced by other basic oxides have been found by various workers in slags in which the CaO to acid-oxide ratio was low. Thus Schneiderhöhn described the appearance of three new constituents, X_1 , X_2 and X_3 , in Hoesch furnace slags, X_1 and X_3 being apparently, from the mode and extent of their occurrence, phosphorus-containing, and X_2 a silicate. X_1 , X_2 and silico-carnotite were found co-existing in some of his slags, while X_2 , X_3 and silico-carnotite co-existed in others. (The difference was not, apparently, simply one of composition, as such constitutional differences were found to exist between slags differing little in composition.) In general, the former combination appears to have occurred in spoon samples taken during the process, while the latter occurred in samples taken from the finished slag which had been cooled in the

mass. Schneiderhöhn suggested that the difference was due to the "heteromorphism" of basic slags, by virtue of which slags of similar composition can, under different conditions, freeze to give different constituents. (The so-called heteromorphism of phosphate slags was at one time the subject of considerable controversy, centring, in particular, round Hilgenstock's attempts to show that steadite and silico-carnotite were simply different forms of $4\text{CaO} \cdot \text{P}_2\text{O}_5$, though it will be noticed that this use of the term differs somewhat from that of Schneiderhöhn.)

It is not yet possible to say definitely what these phases were, though it is significant that they appeared in his slags only when the molecular ratio of CaO to P_2O_5 dropped below about 5/1. Schneiderhöhn concluded that X_1 and X_3 were probably calcium-magnesium silico-phosphates, the latter probably a substituted silico-carnotite from its properties. Both had extremely low citric-acid solubilities. X_2 , he concluded, was probably a calcium-magnesium silicate. A similar compound, apparently a monticellite, was also found by Bainbridge, associated with apparently normal apatite, in a slag containing fluorspar. Scott and McArthur also observed what appeared to be an alteration product associated with one of the silico-phosphates found in some of their slags. It is probably significant that the CaO contents of such slags as shown by their analyses was too low to satisfy completely the requirements of the SiO_2 and the P_2O_5 , so that it is quite possible that this was a "substituted" compound of the type observed by Schneiderhöhn.

Though it has been generally assumed that MgO would be the principal substituent in such compounds, this is by no means certain, and it is likely that FeO and MnO will both be capable of acting in this way. All three oxides are known to form phosphates and to occur as constituents of natural phosphate minerals. They also form monticellites, as discussed earlier. On the whole, very little is known of the systems involved, though part of the system Fe-P-O has been studied by Wentrup⁽¹⁴⁹⁾ and also by Schenck and his co-workers.⁽¹¹⁶⁾

(e) "*Spinel*s" and "*Spinell*oid Materials."

These terms have been used to denote not only true spinels but all compounds formed between Fe_2O_3 and Al_2O_3 and the divalent basic oxides of the slag. Actually, there is some doubt as to whether true spinels will normally occur in basic slags, as they do not, in spite of their characteristic crystalline form, appear to have been identified with certainty. Ferguson has stated that Fe_3O_4 , which is a spinel, never occurs in basic slags. The following two calcium ferrites are described specifically in the literature as occurring in slags.

(1) *Tricalcium Ferrite* ($3\text{CaO} \cdot \text{Fe}_2\text{O}_3$).—Crystals corresponding approximately to this composition, but actually containing appreciable amounts of FeO , MnO , MgO and Al_2O_3 in addition to

CaO and Fe_2O_3 , were isolated from slags by Stead and Ridsdale and by Ferguson. No such compound has been found in the system $\text{CaO}-\text{Fe}_2\text{O}_3$ (Fig. 9(A)) and several suggestions have been made to explain the contradiction, *e.g.*, that a "mixed" ferrite $3\text{RO}.\text{R}_2\text{O}_3$, of which the homogeneity range does not extend to the binary system $\text{CaO}-\text{Fe}_2\text{O}_3$, exists. Nagai and Asaoka,⁽¹⁵⁰⁾ on the other hand, claim to have established that $3\text{CaO}.\text{Fe}_2\text{O}_3$ exists but that it undergoes dissociation at high temperatures into $2\text{CaO}.\text{Fe}_2\text{O}_3$ and CaO . Crook's claim to have established its existence is somewhat doubtful for reasons previously stated (Section VI.(b)). At the present time it is not possible to arrive at a definite conclusion on the subject.*

(2) *Dicalcium Ferrite* ($2\text{CaO}.\text{Fe}_2\text{O}_3$).—The occurrence of this compound in the system $\text{CaO}-\text{Fe}_2\text{O}_3$ is well established (Fig. 9(A)). It was isolated from basic slags by Stead and Ridsdale, and its frequent occurrence in such slags, particularly towards the end of the refining process, is generally accepted. It may be noted that in the presence of Al_2O_3 part of the Fe_2O_3 will be replaced by it (*see* Fig. 10(A)).

(f) *Free Oxides.*

Strongly-magnetic, fern-like crystals, consisting almost entirely, if the Fe_2O_3 content be ignored, of divalent basic oxides including CaO , have been separated from basic slags by Stead and Ridsdale, Ferguson, and Bainbridge, and in all probability correspond to the "free-oxide phase" observed microscopically by Scott and McArthur, Schneiderhöhn and others. The presence of Fe_2O_3 in this phase is not inconsistent with the known data on the relevant systems, since wüstite can exist with over 30% of Fe_2O_3 in solid solution (*see* Fig. 15(A)), while MgO can dissolve very considerable amounts of Fe_2O_3 at high temperatures (Fig. 9(B)). In this latter connection, Bainbridge actually suggested that the oxide phase might be considered as a solution of Fe_3O_4 , FeO and MnO in periclase. With regard to the presence in solution of CaO , in the amounts found by these workers, Fig. 22(D) shows one way in which such solubility might be explained, provided that there is appreciable solubility of CaO in MnO . (There does not appear to be any information available on this point, but it may be noted that the diameter of the manganese ion differs less from that of calcium than do the other two metal ions.) Because of the action of CaO on FeO the system will not be a true quaternary one, and it is necessary to insert the plane of section AXB corresponding to equilibrium between $2\text{CaO}.\text{Fe}_2\text{O}_3$ and metallic iron. As it is possible that solid solutions low in FeO will, over a limited range of compositions, be capable of co-existing with CaO , the plane of

* It may be noted that no indications of the existence of $3\text{CaO}.\text{Fe}_2\text{O}_3$ have been found in cement or dolomite clinkers (*see* Lea and Desch⁽⁶⁶⁾ and also Rait and Goldschmidt⁽¹⁵⁴⁾).

section is not drawn to intersect the solid-solution range on the MgO-CaO-MnO face of the diagram but on a line situated at some distance from this face. To the right of this plane (except for the region subtended by this assumed range of stable solid solutions) CaO , $2\text{CaO.Fe}_2\text{O}_3$, iron and solid-solution compositions along the line of section will co-exist, while to the left of it, but outside the homogeneity range of the solid-solution series, oxide solid solutions, $2\text{CaO.Fe}_2\text{O}_3$ and iron will co-exist. Incidentally if the oxide-phase compositions given by Stead and Ridsdale, and Ferguson and Bainbridge are plotted in terms of their MnO , MgO and FeO contents as shown in Fig. 22(E), it is found that the highest CaO content does occur with the highest MnO content. (This method of plotting, of course, neglects the possible influence on the CaO solubility of Fe_2O_3 dissolved in the oxide phase.) Lines of constant CaO content might possibly run in the direction indicated by the dotted lines, but the three compositions available are, of course, far too few to allow of any definite conclusions being reached. In addition, the possibility of contamination of the analysed samples by other slag constituents cannot be entirely overlooked, particularly when it is remembered that the free oxide occurs presumably as a constituent of a eutectic. (See Addendum below.)

Addendum.—Since the above was written the author has obtained evidence suggesting that, in the presence of CaO , MnO acts in a manner similar to FeO , with liberation of metallic manganese and formation of what is presumably a calcium manganite of lower dissociation pressure than MnO . As a result, mixtures containing 10–20% of CaO have relatively low fusion points, at least as compared with the constituent oxides. If this is correct a certain proportion of the manganese in liquid basic slags will probably exist as a higher oxide than MnO . Such a view has, in fact, already been expressed by Lawrie,⁽¹⁸⁵⁾ and will possibly mean that manganese oxides, like iron oxides, will promote the transfer of oxygen through the slag to the bath. It may also have a bearing on the fact that lime additions can under certain circumstances cause the return of manganese to the bath. This reaction does not necessarily rule out the possibility of some solid solubility of CaO in MnO (*cf.* the case of CaO and FeO), though it is likely to be somewhat more restricted than is indicated in Fig. 22(D). In seeking to account for the compositions of the free-oxide phase reported by Stead and Ridsdale, Ferguson, &c., it is perhaps natural to recall the compounds X and Y postulated by Schenck and his co-workers (*see* Section VI.(b)). Further information on the nature of these phases is required, however.

IX.—PHASE RELATIONSHIPS IN BASIC SLAGS.

A.—*Scheme to Define Phase Fields in Slags.*

The most serious obstacle to the systematic study of the constitution of basic slags lies in the fact that, owing to the number of components present, no adequate diagram portraying phase relationships in the slag as a whole can be constructed. Even in the absence of such a diagram, however, it should be possible to define the various phase fields occurring in terms of their constituent phases whenever the phase relations in a sufficient number of the simpler partial systems of the component oxides (say, up to the quaternary systems) have been elucidated, always provided that no new phase of higher order than those found in the simpler known systems appears in the complete system. This latter difficulty will not necessarily be insurmountable, however, so long as the phase data provided by the simpler systems can be implemented by a sufficient number of observations on the slag as a whole. At the present time knowledge of the partial systems is nothing like complete. (The eight principal components of basic slags will form no fewer than seventy quaternary systems among themselves.) Nevertheless, an attempt to state tentatively the phase fields over part of the composition range covered by basic-furnace slags can be made, and is probably justifiable if for no other reason than that it may serve as a useful basis for further work on the subject. The phase fields presented in Table III. were deduced mainly from a study of the relevant ternary and quaternary systems, aided by the observations on furnace slags discussed above. Use was made of the following generalisations :

(1) The maximum number of phases to be expected in any group of phases forming a phase field of an eight-component slag is 8. In general, however, the number may be less, owing to solid-solution formation.

(2) In each phase group every phase must be capable of co-existing simultaneously with every other phase.

As an example of the procedure adopted, those phase fields of the complete system in which free CaO would occur as a phase may be considered. Examination of the phase diagrams discussed earlier shows that $(\text{MgO}, \text{MnO}).3\text{CaO}.\text{Al}_2\text{O}_3$, $(2\text{CaO}.\text{Fe}_2\text{O}_3, 4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3)$, $3\text{CaO}.\text{SiO}_2$, $9\text{CaO}.\text{P}_2\text{O}_5.3\text{SiO}_2$, $5\text{CaO}.\text{P}_2\text{O}_5.\text{SiO}_2$, $4\text{CaO}.\text{P}_2\text{O}_5$ and metallic iron, the latter formed from CaO and FeO of the slag during freezing, can all co-exist with CaO. (Phases bracketed together can form solid-solution series with one another.) All of these phases cannot co-exist simultaneously with CaO, however, as they cannot all co-exist with each other. Hence subdivision into three groups containing $3\text{CaO}.\text{SiO}_2$ and $9\text{CaO}.\text{P}_2\text{O}_5.3\text{SiO}_2$, $9\text{CaO}.\text{P}_2\text{O}_5.3\text{SiO}_2$ and $5\text{CaO}.\text{P}_2\text{O}_5.\text{SiO}_2$, and $5\text{CaO}.\text{P}_2\text{O}_5.\text{SiO}_2$ and $4\text{CaO}.\text{P}_2\text{O}_5$ is necessary.

Further, each of these groups will in turn have to be again subdivided according to whether $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 - 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ solid solutions or $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 - 3\text{CaO} \cdot \text{Al}_2\text{O}_3$ mixtures occur, *i.e.*, according to whether the ratio of Fe_2O_3 to Al_2O_3 is greater or less than 160/102. There will thus be six phase fields in which CaO will occur.

In the scheme outlined in Table III. the phase fields for fluorspar-free slags are arranged in three columns, *A*, *B* and *C*, representing slags in which the values of the $\text{SiO}_2/\text{P}_2\text{O}_5$ ratio are (*A*) less than 60/142, (*B*) between 60/142 and 180/142, and (*C*) greater than 180/142. To conserve space and avoid repetition, the further subdivision necessary to give the final phase groups has been indicated simply by showing that certain alternative phase groupings are possible. Thus, the three groups given at the top of columns *A*, *B* and *C* each represent two phase fields and thus constitute the six phase fields containing free CaO mentioned above. In each column the CaO content of the slag decreases as the column is descended, while, in general, groups shown on the same level have CaO contents of approximately the same order. Column *D*, which is arranged in similar fashion, gives the phase fields of slags containing sufficient CaF_2 to convert all the phosphate to apatite. The following points may be noted with regard to the scheme :

(1) Extension to lower CaO contents than those shown is hardly possible as yet, for examination of the available data on furnace slags suggests that it is at about this CaO content that "mixed" or substituted silico-phosphates appear, and there are insufficient data to indicate the exact nature and sequence of appearance of these compounds. Also at about this stage the appearance of substituted silicates is to be expected, but the sequence in which these appear is deducible with some certainty from the diagrams now available. Thus, in the absence of phosphates and silico-phosphates the disappearance of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ would coincide with the appearance of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (gehlenite). Subsequently, the disappearance of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ with $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ (monticellite) appearing, and of MgO with $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (akermanite) appearing and forming melilites with gehlenite, would occur, and so on.* (It is to be understood, however, that MgO may not be the only substituent in these compounds.) In apatite-containing slags these changes in the silicates appear to take place prior to any change in the apatite, for Bainbridge reported finding a monticellite associated with apparently normal apatite in such a slag.

(2) According to the phase diagrams there is a possibility that spinels might appear before the substituted silico-phosphates and silicates. Two phase groups containing Fe_3O_4 (denoted F'F) are actually shown in the fifth row of column *D*, but these will probably never occur in furnace slags, as they require a ratio of Fe_2O_3 to FeO

* It might later be found necessary to interpose a phase field containing merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) before that containing monticellite.

TABLE III.—*Phase Assemblages in Solidified Basic Slags.*

[illegible]

greater than 160/72. With the disappearance of C_4AF , however, Fe_3O_4 might appear for lower values of this ratio. Alternatively, $FeO.Al_2O_3$ or $Fe_3O_4-FeO.Al_2O_3$ solid solutions might appear at this stage. ($MgO.Al_2O_3$ could not appear, according to Fig. 12(A), before gehlenite, monticellite, &c.) As stated above, however, the indications are that true spinels do not occur in normal basic slags, so this possibility can be dismissed, at least until evidence to the contrary is obtained. If $CaO.Fe_3O_4$ should be found not to exist, the non-appearance of Fe_3O_4 would mean that the formation of other compounds (gehlenite, &c.) was intervening, or else that the tie $FeO-CaO.Fe_2O_3$ should replace tie $Fe_3O_4-2CaO.Fe_2O_3$ in Fig. 19(D). $CaO.Fe_2O_3$ would then replace $CaO.Fe_3O_4$ in the Table III.

(3) Metallic iron but no FeO is shown to occur in the phase fields in which free CaO occurs. This is consistent with the evidence of the phase diagrams, but is somewhat at variance with the results of analysis of actual slags, since even those which are shown by calculation to contain CaO in excess of the probable requirements of the acids contain according to analysis considerable FeO. Suggestions which might be made are that equilibrium was not attained during the freezing, or that the presence of finely-divided iron resulted in fictitious FeO and Fe_2O_3 contents being reported on analysis. It is probably significant that most of the strongly magnetic particles separated from powdered basic slag by Rogers and Stamm⁽¹⁵¹⁾ were found to contain metallic iron, some of it in the form of relatively large globules, possibly owing to admixture with the metal bath, but some of it in a much finer state of division extending down to, and probably also beyond, the size limit detectable by their microscope. Some of it was also in the form of very thin flakes instead of globules. The matter is somewhat complicated, however, by the fact that FeO can also decompose to give metallic iron below 575° C., though the appearance of the iron particles in the micrographs of those workers hardly suggests this mode of origin.

(4) FeO (wüstite) has been assumed to appear whenever free CaO disappears. The possibility that $3CaO.SiO_2$ (as discussed earlier), and even, perhaps, $4CaO.P_2O_5$, might not be stable in contact with FeO cannot be entirely overlooked. In that case a slight modification of the appropriate phase fields would be necessary.*

* According to a recent paper by Oelsen and Maetz,⁽¹⁸⁶⁾ the system $CaO-FeO-P_2O_5$ contains an area of liquid immiscibility extending from the FeO corner towards the composition of $4CaO.P_2O_5$. From the direction of the tie lines they concluded that the section $FeO-3CaO.P_2O_5$ was a quasi-binary one; $4CaO.P_2O_5$ was apparently much less stable than the orthophosphate in the presence of FeO. It may be noted that in the quaternary system $CaO-Fe-Fe_2O_3-P_2O_5$ the section $CaO-FeO-P_2O_5$ will not be a true ternary one, as it will be overlapped over part of its area at least by the metallic-iron/liquid-slag immiscibility zone, while with some compositions the separation of $2CaO.Fe_2O_3$ and metallic iron on freezing is to be expected. It may be significant that the immiscibility area proposed by those authors

(5) Since the phase fields given are based primarily on the phase diagrams of the partial systems, $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is not included. Modification in this respect may also be necessary (*see* footnote to Section VIII.(e)(1), however).

(6) In stating the various phases occurring certain solid solubilities have been neglected, *e.g.*, the solubility of CaO , SiO_2 and possibly other oxides in $3\text{CaO} \cdot \text{P}_2\text{O}_5$, and the possible solubility of CaO in the free oxides. This will, of course, introduce an approximation into any calculation of slag constitution on the basis of these fields.

B.—Comparison of the Scheme with Actual Observations (Table IV.).

To compare the suggested scheme with the results of actual observations on furnace slags it was used as a basis from which to calculate the constitutions of the slags examined by Scott and McArthur⁽¹⁴⁵⁾ and by Schneiderhöhn,^(77, 147) these being suitable for the purpose as their compositions are fully stated. The results obtained are shown in Table IV., but, unfortunately, the number of comparisons that could be made was somewhat restricted, owing to the fact that a considerable number of the slags were too low in CaO to fall within the range covered by the scheme. Hence, the compositions examined are neither numerous nor varied enough to provide a really satisfactory test.

(a) Scott and McArthur's Slags.

(1) *No. 1.*—The authors found steadite, but the ratio of SiO_2 to P_2O_5 is such as would give at the most only a trace of C_3P . Apart from this, and allowing for the uncertainty of the authors with regard to the exact nature of the ferrites and aluminates (they are described in general terms only), the agreement seems reasonable.

(2) *No. 2.*—The chief discrepancy is that C_4P is predicted, whereas the authors found steadite. The discrepancy is not removed even by assuming a tricalcium ferrite and aluminate, and may arise from the solubility of CaO in the oxide phase suggested above, and in steadite, or else because, for the reasons mentioned above, the reported Fe_2O_3 content was low.

(3) *Nos. 3, 4, 5, 6, 7 and 8.*—These are not given in Table IV. The $\text{SiO}_2/\text{P}_2\text{O}_5$ ratio was over 60/142 and they therefore contained the new silico-phosphate observed by those authors, presumably identical with C_9PS_3 . In addition, however, these slags (with the exception of No. 7) were deficient in CaO relative to the requirements of the acids and would presumably contain substituted compounds. The occurrence of what appeared to be an alteration product associated with the new silico-phosphate in some of the slags was noted by the authors (*see also* Fig. 22(*F*)).

occurs in the composition range in which these effects are most likely to be encountered.

With regard to the stability or otherwise of $3\text{CaO} \cdot \text{SiO}_2$ in the presence of FeO , *see* first footnote to Section VI.(g).

TABLE IV.—*Constitution of Basic Slags.**

	Scott and McArthur. ⁽¹⁴⁵⁾				Schneiderhöhn, ⁽¹⁷⁾ his Table 3.				Schneiderhöhn. ⁽¹⁴⁷⁾	
	Slag 1.	Slag 2.	Slag 9.	Slag 10.	Slag 1.	Slag 4.	Slag 7.	Slag 10.	Slag A.	Slag B.
CaO. %	43.94	44.88	38.23	39.60	51.32	51.30	53.04	53.66	45.87	45.29
P ₂ O ₅ . %	18.24	19.43	6.48	13.08	20.65	19.47	19.65	19.62	20.66	22.10
SiO ₂ . %	7.75	5.80	12.20	14.70	6.50	8.19	4.00	8.14	4.00	9.45
FeO. %	6.98	10.60	23.11	10.41	10.02	9.84	9.69	6.69	14.79	10.80
Fe ₂ O ₃ . %	16.09	5.94	5.92	5.14	3.02	2.65	2.92	2.28	4.86	2.14
MnO. %	3.17	6.81	5.87	8.09	6.99	6.68	6.50	6.24	5.68	5.35
MgO. %	3.56	3.23	3.74	4.34	2.14	2.20	1.88	1.94	3.70	3.74
Al ₂ O ₃ . %	...	2.70	4.15	4.60	0.64	0.88	0.84	0.30	0.84	1.09
<i>Calculated Constitution.†</i>										
CaO. %	...	1.85	10.02	10.50	9.14	3.36	6.27	0.0
C ₂ P. %	...	13.18	13.42	0.22	27.08	0.0
C ₄ P. %	Trace
C ₂ PS. %	62.10	40.80	52.06	65.50	33.27	74.70
Apatite. %	15.70	31.35	47.05	47.05
C ₂ S. %	13.47	21.60	30.80
C ₂ F. %	34.95
C ₂ F. %	9.23	2.72	3.54	2.97	4.08	2.99	5.38	0.84
C ₄ F. %	...	11.13	11.51	...	2.91	2.77	1.46	1.46	3.89	5.29
CF. %	20.10	...	3.83	9.25
CA. %	2.68
C ₂ AS. %	12.35
GMS. %	19.03
FeO. %
MnO. %	32.99	16.18	19.15	18.62	18.07	14.87	24.07	19.29
MgO. %	8.61	23.43
<i>Observed Constitution.‡</i>										
C ₂ PS, steatite, ferrites and aluminates, free oxides.	...	C ₂ PS, steatite, ferrites, spinelloids, free oxides.	Apatite, α-C ₂ S ₂ , spinelloids, free oxides.	Apatite, α-C ₂ S ₂ , spinelloids, free oxides.	C ₂ P, C ₄ P, "oxides."	C ₂ P (trace), "oxides."	Apatite, β-C ₂ S ₂ , "oxides."	Apatite, β-C ₂ S ₂ , "oxides."	C ₂ PS, C ₄ P, ferrites or spinelloids, oxides.	C ₂ PS, ferrites, oxides.

* All figures represent weight percentages.

† C = CaO; A = Al₂O₃; S = SiO₂; P = P₂O₅; F = Fe₂O₃; F' = FeO.

(4) *Nos. 9 and 10.*—Fluorspar had been added to both these slags, and both contained apatite and C_2S (apparently α), as well as spinelloids and oxides.

(5) *No. 11.*—This is not given in Table IV., as it was deficient in CaO. It had very low P_2O_5 and resembled fluorspar-containing slags in containing C_2S , this being associated with the new silico-phosphate. This agrees with the relationships indicated in Fig. 22(F), on which the composition of this slag is plotted.

(b) *Schneiderhöhn's Slags (1931 Paper⁽⁷⁷⁾).*

(1) *Bessemer Slags (Table 3 of Original Paper).*—Four slags, three samples of each being cooled by different means, were studied. Only the slowly-cooled samples 1, 4, 7 and 10 are considered here, as the differences caused by the method of cooling were confined to differences in crystal size and in the degree to which the formation of hydroxy-apatite had occurred during cooling. Schneiderhöhn described the ferrites, aluminates and free oxides in general terms as oxides. On comparing predicted and observed constituents it is seen that he describes $\beta\text{-}2CaO.SiO_2$ as occurring in slags 7 and 10 whereas $3CaO.SiO_2$ is predicted in these slags. This may be due to the absence of a field of crystallisation from the liquid state of $3CaO.SiO_2$ in these slags. Free CaO is predicted in all four slags, whereas none was observed, apart from some that occurred as a fine dispersion in the $4CaO.P_2O_5$ crystals as a result of hydration with formation of hydroxy-apatite during cooling. This supports the suggestion that CaO may be soluble in some of the other phases, or else that the reported Fe_2O_3 contents were too low.

(2) *Hoesch Slags (Table 5 of Original Paper).*—Only slag 1 of this series had no CaO deficiency. Slag 2 had a small deficiency, and all the remaining slags had a large deficiency, and it was in these latter that Schneiderhöhn observed the new and presumably substituted compounds X_1 , X_2 and X_3 . These slags have not been given, therefore, in Table IV., but they are shown plotted in Fig. 22(F). Prediction of the constituents of slag 1 agrees with Schneiderhöhn's observations, except that he observed C_4P associated with silico-carnotite. According to the SiO_2/P_2O_5 ratio indicated by his analysis this would appear to be impossible, as C_9PS_3 and silico-carnotite should occur. This is also confirmed by Fig. 22(F).

(c) *Schneiderhöhn's Slags (1928 Paper⁽¹⁴⁷⁾).*

The predicted constitution is in reasonable agreement with that author's observations, and also with the results of his attempts to determine the amounts of the various constituents by utilising their varying solubilities in dilute hydrochloric acid. Thus, he found that slag *A* contained 32.03% of C_5PS and 27.04% of C_4P , while slag *B* contained 75.19% of C_5PS and no C_4P . Further, he found 10.46% of CaO associated with the oxides in slag *A* (i.e., CaO not combined

with either SiO_2 or P_2O_5), whereas there was only 1.65% of such CaO in slag B.

(d) *Graphical Representation of the Slags in Table III.*

In studying the constitution of fluorspar-free slags the author has generally found it informative to plot them in terms of their CaO, P_2O_5 and SiO_2 contents on the ternary diagram given in Fig. 14(B). The result of plotting Scott and McArthur's and Schneiderhöhn's slags in this way is shown in Fig. 22(F); an indication is at once obtained as to whether a slag should contain calcium phosphate and C_5PS , C_5PS alone, C_5PS and C_9PS_3 , C_9PS_3 alone, or C_9PS_3 and calcium silicate. Such a plot will not, however, indicate whether the calcium phosphate is C_4P or C_3P , or whether the silicate is C_3S or C_2S , the reason being that it makes no allowance for the CaO requirements of the Fe_2O_3 and Al_2O_3 , nor will it indicate whether the slag contains excess CaO or a slight deficiency. Larger deficiencies, such that the CaO alone is insufficient to satisfy the requirements of the SiO_2 and P_2O_5 , will, however, be indicated, as the plot will then lie to the right of the join $\text{C}_3\text{P}-\text{C}_2\text{S}$. Scott and McArthur's slags Nos. 3, 4, 5, 6, 8 and 11 and all Schneiderhöhn's Hoesch slags except No. 1 show a large deficiency of this kind.

In the same way slags to which sufficient fluorspar to convert all the phosphate to apatite has been added can be considered in terms of Fig. 22(C). Such slags are in general simpler, as they will consist of apatite and calcium silicate, C_3S or C_2S , or, if there is a deficiency of CaO, substituted silicates such as CMS.

The constitution of basic slags has also been discussed in a more general fashion than the above by Wilson,⁽¹⁵²⁾ Colclough,⁽¹⁵³⁾ Herty,⁽¹²⁷⁾ Cook,⁽¹³³⁾ and by Dodd and Green.⁽¹⁵⁴⁾

X.—FUSIBILITY-COMPOSITION RELATIONSHIPS.

With basic slags, as with acid, fusibility relationships will impose definite limits on the range of compositions that can be used in the furnace. No single diagram for the complete slag system can, of course, be constructed, but the diagrams of the binary and ternary systems of the component oxides give ample indication that this should be so, as CaO, MgO and MnO, though they give low-melting eutectics with the principal acid oxides, themselves have high melting points. The existence of a limit to the CaO content that can be carried is of particular importance, because, where much phosphorus has to be removed from the metal, as high a CaO content as possible will generally be desired. The use of fluorspar to thin high-lime slags is itself testimony to this. A lower limit as regards the concentration of this oxide can also be considered to exist, as, if the slag is too low in CaO (or in basic oxides in general) excessive corrosion of the hearth will result. Macnair⁽¹³⁵⁾ considered that basic slags could be regarded as approaching a state of saturation, or

possibly of limiting viscosity, with increasing CaO content.* Slags too far removed from this limiting condition would automatically tend to approach it by dissolving CaO from the furnace banks. In practice this is prevented from becoming excessive by the frequent additions of lime or limestone made to counterbalance the dilution caused by the continuous entrance of P_2O_5 , SiO_2 , MnO , FeO , &c., into the slag. An important property of any slag is thus its capacity to dissolve CaO. This property should in theory be definable in terms of the proportions of the other oxides in the slag, but in actuality lack of knowledge of the complete slag system makes this impossible. Useful information regarding the solubility of CaO in slags belonging to a good many of the simpler systems formed by the slag components can, however, be obtained from the relevant thermal equilibrium diagrams. Thus, Macnair used data provided by the thermal equilibrium diagrams of the systems $CaO-SiO_2$ and $FeO-SiO_2$ as a basis for his discussion of the factors limiting the composition of basic slags. From an examination of the diagrams now available the following points emerge :

(1) *Figs. 8(D), 1(C), 9(A) and 14(A).*—The amounts of CaO that can be dissolved by $CaO-Al_2O_3$, $CaO-SiO_2$, $CaO-Fe_2O_3$ and $CaO-P_2O_5$ slags at $1600^\circ C.$ are approximately 61%, 58%, 55% and 50%, respectively.

(2) *Figs. 19(B) and 19(C).*—Estimation of the solubility of CaO in liquid FeO is hampered by the lack of an exact diagram and is furthermore complicated by the fact that dissociation of FeO occurs with liberation of iron. As a consequence of this latter, the compositions of CaO-saturated $CaO-FeO$ slags will lie along the suggested trough *BEF* of Fig. 19(C). At $1600^\circ C.$, according to the indications provided by Fig. 19(B), the CaO content at saturation in this trough should apparently lie between 60% and 70%, the slag being then saturated with iron as well as with CaO.

(3) *Fig. 21(B).*—This diagram, in so far as it is valid, being only a fusion-point diagram, indicates that iron oxide heated in air has about the same fluxing power for CaO as has SiO_2 , and that the effect of the two together is roughly additive.

(4) *Fig. 3(A).*—The trend of the isotherms shows that the addition of FeO, in amounts up to about 40% at least, to $CaO-SiO_2$ slags decreases quite markedly the CaO content at saturation. This is contrary to Macnair's assumption that FeO would increase the capacity of $CaO-SiO_2$ slags for CaO. In

* For the purposes of this discussion a slag is regarded as saturated with CaO at any temperature when it cannot dissolve any more of that oxide at that temperature, irrespective of whether CaO itself or a compound of CaO is then in equilibrium with the liquid slag. A $CaO-SiO_2$ slag saturated with CaO at $1600^\circ C.$, for instance, is in equilibrium with $2CaO.SiO_2$. (Cf., however, Addendum to Section X. below.)

the vicinity of the CaO-FeO edge, however, large lime solubility is to be expected. (Cf. Addendum to Section VI.(g).)

(5) *Fig. 11(D)*.—The addition of up to 20% of Al_2O_3 to CaO-SiO₂ slags causes the lime solubility at 1600° C. to decrease. With 20% of Al_2O_3 a lime-saturated ternary slag contains only 50% of CaO at this temperature. At higher Al_2O_3 contents the lime solubility increases again, but the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios at which this occurs are much higher than are normally found in furnace slags.

(6) *Fig. 10(A)*.—The solubility of CaO in CaO-Fe₂O₃ slags at 1600° C. is increased by the addition of Al_2O_3 , the CaO content at saturation being greater than 60% for slags on the CaO-4CaO. Al_2O_3 .Fe₂O₃ join. It remains high for molar ratios of Al_2O_3 to Fe₂O₃ greater than this.

(7) *Fig. 13(D)*.—The surface of lime saturation at 1600° C. in the quaternary tetrahedron of the system CaO-5CaO.3 Al_2O_3 -4CaO. Al_2O_3 .Fe₂O₃-2CaO.SiO₂ enters the tetrahedron *via* the C₂S-C₄AF-C₅A₃ face, intersecting the C₄AF-C₂S edge at about 33% of C₂S and the C₅A₃-C₂S edge at about 37% of C₂S, and emerges on the CaO-C₅A₃-C₄AF face, intersecting the CaO-C₄AF edge at about 30% of CaO and the CaO-C₅A₃ edge at approximately 25% of CaO. (These compositions are in terms of the ranges covered by the diagram, not in terms of the component oxides.) Comparison of *Figs. 11(D), 10(A) and 13(D)* indicates that the addition of Al_2O_3 to a slag containing appreciable 2CaO.Fe₂O₃ should tend to raise the CaO content at saturation. If the Fe₂O₃ content is low, however, some decrease may occur. The presence of Al_2O_3 or of Al_2O_3 and Fe₂O₃ in large amounts relative to the SiO₂ content will increase the solubility. In normal slags the first-mentioned effect should predominate.

(8) *Fig. 5(A)*.—MgO forms a eutectic with CaO, and at first sight it might be thought that the presence of MgO, by increasing the fusibility, might increase the lime solubility in basic slags. This is not necessarily the case, however, and in CaO-MgO-SiO₂ slags the opposite effect occurs, as shown by the trend of the 1600° C. isotherm of *Fig. 5(A)*. With 20% of MgO a lime-saturated ternary slag will contain about 44% of CaO only at 1600° C., and will be unable to carry sufficient CaO at this temperature to satisfy the requirements of the SiO₂, so that monticellite will appear on freezing.

(9) *Fig. 8(F)*.—MgO also lowers the CaO content at saturation of CaO-MgO- Al_2O_3 slags at 1600° C., *e.g.*, with 10% of MgO a ternary slag contains only 55% of CaO at saturation.

The indication afforded by the two last-mentioned items that MgO may decrease the solubility of CaO in furnace slags is of some

significance, as MgO is unavoidably picked up by the slag from the hearth refractory. (The slag will tend to become saturated with MgO as well as with CaO in the furnace, though in most slags it appears unlikely that saturation with the former oxide will actually be reached. In some of the low-lime slags found in German practice it may be.) In many slags, of course, according to the evidence at present available, the MgO will occur principally, if not entirely, in the free-oxide phase, but even then reasons can be adduced for supposing that its effect on the slag may be similar, for, as the concentration of MgO in solid solution in this phase increases, its freezing point will rise. As a consequence the freezing temperatures in any eutectiferous systems which this solid-solution series may form with other constituents of the slag will rise as the MgO content increases. This may well cause a decrease in the CaO content of the slag at saturation. Incidentally, MnO , another basic oxide of high melting point, which has the same modes of occurrence in basic slags as MgO (like the latter, it forms a compound of the monticellite type), may, it is reasonable to suppose, have a similar influence.

Support for these conclusions is provided by the findings of Schleicher,⁽¹⁵⁵⁾ who pointed out that the sum of the CaO , MgO and MnO contents in basic-furnace slags tended to have a constant value. In one series of twenty-nine slags he found the mean value of this sum to be 61.4%, while in another series, which he reproduced from a paper by Janitzky,⁽¹⁵⁶⁾ the mean value was 61.53%. Schleicher demonstrated this relationship by plotting the MnO contents against the $\text{CaO} + \text{MgO}$ contents for the slag compositions given in his paper, when a linear relationship was revealed, though, as might be expected, there was considerable scattering of the plotted points about the mean straight line. Actually, if the views expressed above are correct, it would seem as logical to plot CaO against $\text{MgO} + \text{MnO}$. In Fig. 23(A) this latter method of plotting is adopted, the slag compositions being from Schleicher's paper, and from Table III. of the paper on "British Open-Hearth Data and their Correlation" of the Iron and Steel Institute Symposium on Steelmaking, together with the finishing slag compositions given in Table V. of the present paper; the latter are taken mainly from the literature. There is somewhat less scattering of the plotted points by this method than by Schleicher's method, and there is also better differentiation between spar-containing and spar-free slags, the former tending, on the whole, to lie to the upper side of the mean straight line AB . Further, by this method of plotting it is found that the points corresponding to spar-containing slags tend to fall within the lower range of MgO - MnO contents only, and, in fact, all but two of the spar-containing compositions fall within the area bounded by the curve CDE . Again, if the spar-containing slags are neglected the mean curve through the plotted points will deviate to the lower side of AB in this range, giving somewhat lower mean values of the sum $\text{CaO} + \text{MgO} + \text{MnO}$, while, if only the spar-

containing slags were considered in this range the mean curve would deviate upwards. The inference is apparently that though MgO and MnO raise the freezing point of the slag (bring it nearer saturation) they do so to a less marked extent than does CaO itself. Hence, though the sum $\text{CaO} + \text{MgO} + \text{MnO}$ approximates to a constant value, there is actually a tendency for it to be somewhat higher when the MgO + MnO content is high than when it is low. (Schleicher's mean curve, though linear, indicates the same difference between high and low MnO contents.) The use of spar is apparently mainly necessary in this low MgO + MnO range when it is desired to carry high CaO contents for efficient dephosphorisation. Inci-

TABLE V.—*Basic Slag Compositions (Finishing Slags).*

SiO_2 , %	CaO, %	P_2O_5 , %	MnO, %	MgO, %	FeO, %	Fe_2O_3 , %	Al_2O_3 , %
<i>Without Spar.</i>							
11.4	42.5	9.2	7.8	7.4	15.6	3.9	1.0
23.2	38.4	2.5	13.6	7.8	8.5	3.4	1.5
7.9	47.3	13.9	6.4	5.0	7.6	8.2	...
9.9	46.0	9.0	7.9	4.7	14.7	4.3	...
8.4	37.5	14.1	7.2	13.9	8.4	7.3	...
13.2	40.1	7.5	10.9	7.5	18.1	...	3.0
9.4	41.9	14.7	7.3	5.8	8.6	6.6	...
20.5	41.7	0.8	10.9	8.7	10.3	2.7	2.2
15.9	47.8	3.7	9.1	6.0	11.4	3.1	2.3
19.1	42.9	2.6	6.6	6.1	15.5	2.5	...
7.6	47.5	5.0	9.3	6.9	16.2	5.2	2.2
20.4	45.2	1.9	10.3	9.7	8.2	2.5	1.4
<i>With Spar.</i>							
9.0	46.8	16.4	4.6	5.0	8.6	5.3	1.9
12.0	51.0	4.5	7.0	5.5	11.0	5.0	2.0
17.8	51.5	1.4	6.2	6.6	10.4	1.9	2.0
16.0	54.0	1.2	5.2	4.9	13.1	3.3	2.0
16.2	52.5	1.2	6.7	6.6	12.1	2.4	1.8
17.8	58.2	1.9	7.0	5.0	6.6	1.3	1.9
11.8	53.9	7.3	6.0	6.7	9.4	2.0	1.4
13.7	53.8	3.0	9.2	4.8	9.5	4.1	1.1

dentally, where high CaO has to be carried dolomite hearths should have a definite advantage over magnesite ones, in that they will in general give lower MgO contents in the slag. (*See Addendum below.*)

Schleicher also pointed out that the sum of the SiO_2 , P_2O_5 and iron-oxide contents of basic slags tended to be constant. This may probably be regarded as following from the constancy of the $\text{CaO} + \text{MgO} + \text{MnO}$ content, since the sum of the contents of Al_2O_3 and any remaining constituents of the slag are generally of the order of 2–3% only. In general the fluorspar-free compositions plotted in Fig. 23(A) satisfy this relationship fairly well, though it was noticed in plotting them that there was a tendency for the $\text{CaO} + \text{MgO} + \text{MnO}$ content to be lower when the P_2O_5 content was high and *vice versa*. This tendency, which is revealed in Fig. 23(B), where the spar-free compositions are plotted on a ternary diagram in terms of their

SiO_2 , P_2O_5 and iron-oxide contents, can perhaps be attributed to the fact that, as indicated by the thermal equilibrium diagrams, P_2O_5 is less of a flux for CaO than either SiO_2 or iron oxide.

It is perhaps obvious that any relationship based on the existence of fusibility or fluidity limits to the slag compositions attainable in

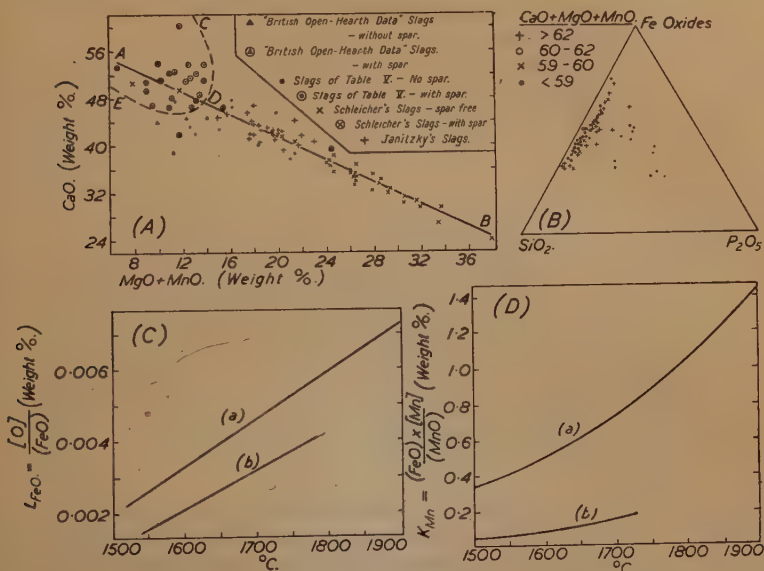


FIG. 23.—(A) Relationship between CaO Content and $\text{MgO} + \text{MnO}$ Content of Basic Slags (weight percentages). (B) Variation of $\text{CaO} + \text{MgO} + \text{MnO}$ Content of Basic Slags with Variation in the Iron Oxide, SiO_2 and P_2O_5 Contents (weight percentages). (C) Variation of L_{FeO} with Temperature for (a) FeO - MnO slags (Körber⁽⁹⁵⁾), (b) FeO - MnO - SiO_2 slags saturated with SiO_2 (Körber and Oelsen⁽¹⁶⁷⁾). (D) Variation of K_{Mn} with Temperature for (a) FeO - MnO slags (Körber and Oelsen⁽¹⁶⁸⁾), (b) FeO - MnO - SiO_2 slags saturated with SiO_2 (Körber and Oelsen⁽¹⁶⁷⁾).

practice must be subject to considerable variations as between individual slags, as it is unlikely that conditions giving "workability" will be highly critical, and such factors as the temperature of the furnace, the method of operation employed and the type of steel produced may all operate to cause variations from any established mean. A claim that the last-mentioned of these factors has an appreciable influence on Schleicher's relationship was made by Sonntag and Wark,⁽¹⁵⁷⁾ who stated that the $\text{CaO} + \text{MgO} + \text{MnO}$ content is always appreciably higher in slags from high-carbon heats than in those from low-carbon heats. It is not difficult to assign reasons for this in terms of the reactions occurring in the furnace. In terms of slag fluidity it may arise from the desire for a thicker,

more inert slag to facilitate control over a bath which has to be "caught" at higher carbon contents. Hay, Ferguson and White⁽¹³⁴⁾ noticed a similar difference between acid slags from high- and low-carbon heats.

In conclusion, when a relationship has been established by methods which are essentially statistical in nature, as has the foregoing, it may well happen that differences of opinion may be possible as to the underlying cause or causes. In the discussion on Schleicher's paper several different interpretations of his relationship were put forward. He himself apparently considered the operative influence to be the effect of CaO on slag "thickness." As shown above, this is apparently not inconsistent with the evidence provided by the thermal equilibrium diagrams of the simpler systems of the slag-forming oxides. At first sight, however, it may seem somewhat surprising that slags as low in CaO as some of those given by Schleicher should be approaching a limiting concentration of this oxide, but an examination of the compositions of these low-lime slags shows that this may well be the case, for they will all, apparently, contain a high proportion of high-melting CaO compounds. Thus, Schleicher's slag No. 1—the analysis of which is 22.74% SiO_2 ; 11.18% FeO ; 2.20% Fe_2O_3 ; 27.95% MnO ; 23.70% CaO ; 9.80% MgO ; 1.14% Al_2O_3 ; 0.44% P_2O_5 —will apparently contain about 4% of $2\text{CaO} \cdot \text{SiO}_2$, 56% of monticellite (containing MnO and probably also some FeO as well as MgO) and over 30% of the free-oxide phase, while slag No. 5—composition 18.85% SiO_2 ; 12.73% FeO ; 3.05% Fe_2O_3 ; 19.70% MnO ; 34.35% CaO ; 6.67% MgO ; 2.02% Al_2O_3 ; 1.45% P_2O_5 —will probably contain about 46% of $2\text{CaO} \cdot \text{SiO}_2$, 6% of monticellite and 36% of free-oxide phase. Incidentally, both the freezing temperature and the bulk of the free-oxide phase will in general increase with the $\text{MgO} + \text{MnO}$ content of the slag. This will tend to compensate for any reduction in the freezing points and in the amounts of the lime compounds, and has possibly an appreciable influence on the freezing temperatures of the slag. If the freezing points of FeO , MgO and MnO are taken as being 1370° , 1785° and 2800°C. , respectively, and if it be assumed that the freezing point is a linear function of the composition over the solid-solution series formed by these oxides (probably a reasonable assumption for the purposes of an approximation), then the melting point of any composition will be given by the equation :

$$\text{Freezing point} = (1370 + 14.3 \text{ MgO} + 4.2 \text{ MnO}) ^\circ \text{C.},$$

where MgO and MnO represent the weight percentages of these oxides in the solid solution. When this equation is applied to the free-oxide phase of slags in which there is sufficient CaO to ensure that substantially all of these oxides will be free (the relative proportions of MgO , MnO and FeO entering into combination with SiO_2 in low-lime slags cannot be estimated), it indicates freezing

points ranging generally between 1700° and 1900° C.* This, of course, takes no account of the possibility that some CaO and Fe_2O_3 may also be present in this phase, but is probably sufficient to indicate that the free-oxide phase is in general a high-freezing one. It may thus separate early during the freezing of basic slags, and this is, in fact, suggested by the fact that this constituent in some of Schneiderhöhn's micrographs has a distinctly dendritic appearance. Generally it would appear that silicates, silico-phosphates or phosphates separate out first, being followed probably by the free oxides, while the more fusible constituents separate only when eutectics of higher order are reached.

Addendum.—Spar-free slags can possibly be divided into two types: (1) Those with high $\text{MgO} + \text{MnO}$, low CaO and low P_2O_5 , and (2) those encountered in the making of low-carbon heats in normal British practice, in which the $\text{MgO} + \text{MnO}$ content is generally low, the CaO content correspondingly high (though not generally as high as in spar-containing slags), the P_2O_5 content rather high and the iron-oxide content high. In the first type high CaO is not required, as the P_2O_5 to be "fixed" in the slag is low. In the second type, owing to the high iron-oxide content, the $\text{SiO}_2 + \text{P}_2\text{O}_5$ content is correspondingly low, so that the proportion of the CaO in the uncombined state is probably high. This is probably the chief reason why fluorspar can be dispensed with most frequently in the making of low-carbon heats. The relatively high fluxing power of iron oxides for CaO is also a factor, but the analyses of such slags show that it is not comparable with that of spar. Attention may be drawn to the conception developed by Körber and Oelsen,⁽¹⁷⁸⁾ who utilise the thermal equilibrium diagrams of the various systems formed by CaO with the other slag-forming oxides to estimate the activity of CaO in various types of slags at steel-making temperatures. For example, in a CaO-FeO slag saturated with CaO at, say, 1600° C. the activity of the CaO in solution will be at its maximum possible value and equal to that of the solid CaO in equilibrium with the slag. A CaO-saturated CaO- SiO_2 slag at 1600° C., however, is in equilibrium not with CaO but with $2\text{CaO} \cdot \text{SiO}_2$, and the activity of the CaO in solution is only equal to that of the CaO in solid $2\text{CaO} \cdot \text{SiO}_2$. Similar considerations will apply to the complete slag system.

XI.—THE VISCOSITIES OF OPEN-HEARTH SLAGS.

In the foregoing Sections the question of limiting slag composition has been discussed generally in terms of fusibility limits or saturation limits at steelmaking temperatures. In practice it will be fluidity rather than fusibility as such which will determine the work-

* In the case of slags high enough in CaO an error would result in that, owing to the presence of metallic iron formed on freezing, the reported FeO would be too high.

ability of a slag as judged by the furnace operator, and, as shown by the work of McCaffery,⁽¹⁵⁸⁾ Rait and Hay,⁽¹⁵⁹⁾ Rait, M'Millan and Hay,⁽¹⁶⁰⁾ &c., there is no direct relation between fluidity at a given temperature and fusibility, *e.g.*, at temperatures above the liquidus a eutectiferous series will not in general have a minimum viscosity at the eutectic composition. When, however, the temperature at which the viscosities are measured is not wholly above the liquidus temperature of the system, an increase of viscosity, generally a marked one, is to be expected whenever the liquidus is crossed, this corresponding to the formation of a two-phase liquid-solid system. In some cases the viscosity begins to increase before the liquidus is actually reached, this being attributable, possibly, to molecular association in the liquid state prior to the actual separation of a solid phase. Data relating to the behaviour of actual furnace slags are somewhat scarce, but there are sufficient indications of the general relationships involved. Thus in basic-oxide/silica systems a characteristic feature is the progressive increase in viscosity with increasing SiO_2 content. In the system MnO-SiO_2 , according to the data of Rait, M'Millan and Hay, this increase is very marked even over the range 35–40% of SiO_2 , and it will presumably become increasingly rapid as saturation is approached. On the viscosity curves for the system CaO-SiO_2 , as given by the same authors, there is apparently a discontinuity in the form of a minimum near to the composition CaO.SiO_2 , but from 52% of SiO_2 upwards the viscosity appears to increase progressively with the SiO_2 content. Acid slags can, therefore, be considered as increasing continually in viscosity as the SiO_2 content is raised, and the indications are that a condition of limiting viscosity will be reached at or at least near to the saturation point (*cf.* also Herty and Fitterer⁽¹⁶¹⁾ and Matsukawa⁽¹⁶²⁾). Incidentally, similar viscosities occur at much higher SiO_2 contents on the CaO-SiO_2 curves than on the MnO-SiO_2 curves. This is in agreement with the relationships indicated in Fig. 22(A).

In the case of basic slags the position would appear to be somewhat different, as increasing the CaO content towards saturation might in general be expected to decrease the viscosity. There are, however, indications that some increase in viscosity may occur with increasing CaO when the slag is near to saturation with this oxide, and there is a very marked increase when the saturation point is actually reached. Evidence of both these effects is provided by the work of McCaffery, and of Rait, M'Millan and Hay on the systems CaO-SiO_2 , $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. The first-mentioned effect is generally relatively small, however, and the viscosities attained up to the saturation point are appreciably lower than will be the case for acid slags at saturation. It would appear, therefore, that with basic slags a limiting viscosity may not be attained till saturation is actually reached, or perhaps even passed to a slight extent. With regard to the action of fluorspar on basic

slags, this appears to be twofold: It increases the fluidity of a given slag, and it also lowers its freezing point very markedly, so that at any temperature the amount of CaO required to saturate the slag is increased.* Further information on slag viscosities can be obtained from a recent review by Rait and Green.⁽¹⁶³⁾

XII.—THE CHEMISTRY OF THE LIQUID SLAG.

Our present knowledge of the chemistry of liquid slags may be said to be tentative only. Definite evidence concerning their constitution is necessarily harder to obtain for liquid slags than for solid slags, in which the crystalline constituents can usually be identified. There is, however, abundant evidence to suggest that compounds do occur in liquid slags. The investigations by Feild and Royster⁽¹⁶⁴⁾ on the viscosity-composition relationships of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags, for instance, showed that decided constitutional influences were operative in their melts. Similar evidence is provided by the slag-viscosity data of Rait and Hay,⁽¹⁵⁹⁾ Rait, M'Millan and Hay,⁽¹⁶⁰⁾ Preston,⁽¹⁶⁵⁾ McCaffery⁽¹⁵⁸⁾ and others. In addition, purely chemical evidence is forthcoming, as it is difficult to explain the stabilising effect of CaO on P_2O_5 , CaO on Fe_2O_3 and SiO_2 on FeO in liquid slags without assuming that stable compounds involving these oxides are formed. Many statements are to be found in the literature as to the probable compounds occurring, but often these are little more than mere assumptions with little evidence to support them. Colclough⁽¹⁵³⁾ early tried to group the oxides found in basic slags into stable combinations in an endeavour to provide a rational explanation for the behaviour of such slags in the furnace. He concluded that the CaO combined primarily with the P_2O_5 and SiO_2 to form $4\text{CaO.P}_2\text{O}_5$ and 2CaO.SiO_2 , respectively, while CaO in excess of the amount required for this combined with Fe_2O_3 to form calcium ferrites. Only if the CaO content of the slag was low could appreciable manganese silicate be formed. He states that the action of CaO in displacing MnO from manganese silicate in basic slags is exactly analogous to its action in acid slags, in which it displaces FeO from ferrous silicate. Krings and Schackmann⁽¹²⁵⁾ have concluded that it is the metasilicates of CaO, MnO and FeO that occur in liquid slags, their stabilities decreasing in that order.

* Another probable effect of spar is deduced by Körber and Oelsen,⁽¹⁷⁸⁾ who report that FeO-CaF_2 mixtures melted at $1400\text{--}1450^\circ\text{C}$. separate into two immiscible liquid layers, of which the CaF_2 -rich layer contains only about 2% of FeO. The activity of this 2% of FeO dissolved in CaF_2 will, thus, be equal to that of the 98% of FeO in the other layer. The interatomic forces between FeO and CaF_2 which give rise to this immiscibility and to the enhanced activity of the FeO in the CaF_2 -rich layer will still persist when the two substances are present in more complex slags, and hence the FeO should show increased activity in the presence of CaF_2 , i.e., it should be more active as an oxidiser than the same amount of FeO in spar-free slags.

Tammann and Oelsen.⁽¹⁶⁶⁾ on the other hand, concluded that 2CaO.SiO_2 was the most stable silicate in basic slags.

More recently an attempt has been made by the author⁽⁸⁴⁾ to show that relationships observed in the study of Fe_2O_3 dissociation equilibria in liquid melts (*see* earlier) could be accounted for with reasonable accuracy on the basis of the simple law of mass action if it were assumed that the melts could be regarded as ideal solutions in one another of various compounds known to exist in solid slags, these compounds being, however, in general partially dissociated into their constituent oxides. It was found that the curves of Fig. 16(B) for pure iron-oxide melts could be reproduced quite closely on the assumption that FeO , Fe_2O_3 and Fe_3O_4 were all present in the melts, the relationships between them being conditioned by the reversible reactions :

$$\text{Fe}_2\text{O}_3 = 2\text{FeO} + \frac{1}{2}\text{O}_2, \text{ whereby } k_1 = \frac{(\text{FeO})^2 \sqrt{\text{O}_2 \text{ Pressure}}}{(\text{Fe}_2\text{O}_3)}$$

$$\text{and } \text{Fe}_3\text{O}_4 = \text{FeO} + \text{Fe}_2\text{O}_3, \text{ whereby } k_2 = \frac{(\text{FeO}) \times (\text{Fe}_2\text{O}_3)}{(\text{Fe}_3\text{O}_4)}$$

where all concentrations are expressed as molar fractions. (Actually, three equations linking the three oxides of iron can be written, but any two of these are sufficient to define the equilibrium completely.) In similar fashion the effect of CaO on the dissociation of Fe_2O_3 could be accounted for on the assumption that $\text{CaO.Fe}_2\text{O}_3$ and $2\text{CaO.Fe}_2\text{O}_3$ were formed in the melts. The effect of SiO_2 , on the other hand, was due principally to the formation of FeO.SiO_2 , 2FeO.SiO_2 being almost entirely dissociated, while with CaO and SiO_2 together in the melts the primary tendency was to form CaO.SiO_2 and to a lesser extent 2CaO.SiO_2 (the latter compound being more highly dissociated than the former). By application of the dissociation constants thus evaluated to established data on the influence of slag composition on slag-metal equilibria it was found possible to evaluate dissociation constants for the manganese silicates and also to show that the observed variations in the slag-metal constants could be reasonably well explained in terms of the concept of slag constitution thus developed. The results obtained indicate that CaO.SiO_2 , MnO.SiO_2 and FeO.SiO_2 are the principal silicates occurring in liquid slags. The stabilities of these compounds decrease in the order given, MnO.SiO_2 being slightly and FeO.SiO_2 markedly less stable than CaO.SiO_2 . Hence, CaO can readily replace FeO from combination with SiO_2 , *e.g.*, CaO additions to acid slags will set free an appreciable proportion of the combined FeO . MnO.SiO_2 is much less affected by the presence of CaO , but in basic slags in which the CaO is considerably in excess of the MnO little MnO.SiO_2 should be present.

The utilisation of slag-metal equilibrium data to throw light on the question of slag constitution is based on the following considerations: It can be assumed that the relationships between slag and

metal are governed, to a fairly close approximation at least, by the ideal solution laws. Thus, the distribution of FeO between the two media is known to be according to the partition law, while it has also been possible to evaluate equilibrium constants for the various slag-metal reactions. In practice, however, all such constants are usually expressed in terms of the total weight percentages in the slag and metal of the reactants involved. Mass-action requirements, of course, stipulate that only concentrations of chemically-free reactants should be considered in evaluating equilibrium constants, but it is not generally possible to do this for slag and metal reactions, as there is no direct way of determining what proportion of any reactant is free. Only the total concentrations as got from chemical analysis are available. Hence, only when no compound formation is possible in the slag, *e.g.*, when it is composed of basic oxides only, will the constants so evaluated be true mass-action constants. (It is assumed as a working hypothesis that none of the reactants in the metal phase forms compounds.) When acid oxides are also present in the slags (assuming that stable compounds are formed) these "constants" will no longer be true mass-action constants, and will, in fact, probably have values differing from those for simple basic-oxide slags. This is, of course, found to be the case. The FeO partition coefficient (denoted by the symbol L_{FeO} and expressed commonly as $[\text{O}]/(\text{FeO})$ (where the round brackets indicate the concentration in the slag, and the square brackets the concentration in the metal)), is appreciably smaller for acid than for basic slags, as shown in Fig. 23(C), which is based on data given by Körber⁽⁹⁵⁾ and by Körber and Oelsen⁽²⁶⁾ for (a) FeO-MnO slags, and (b) FeO-MnO-SiO₂ slags saturated with SiO₂. This is in keeping with the view that all of the FeO in acid slags is not chemically free. A similar difference is found in the case of the slag-metal equilibrium constant for the manganese reaction, *viz.* :

$$K_{\text{Mn}} = \frac{(\text{FeO})[\text{Mn}]}{(\text{MnO})}.$$

The curves of Fig. 23(D) show Körber and Oelsen's values for K_{Mn} as calculated in the usual way for the above two types of slag.^(26, 167) If this difference is wholly due to the presence of silicates of FeO and MnO in the acid slag, then, presumably, the true mass-action values of L_{FeO} and K_{Mn} will be the same for both types of slag. Further the (a) curves of Figs. 17(A) and 17(B) will give the true values, since no compounds would be present in the basic-oxide slags. In applying these conclusions to the case of equilibrium between the metal and an acid slag, we can write :

$$(\text{FeO}) = \frac{[\text{O}]}{L_{\text{FeO}}},$$

where (FeO) is the concentration of free FeO in the slag, [O] is the concentration of oxygen in the metal and L_{FeO} is the true value of the partition coefficient. Thus, the concentration of free FeO in the

slag can be calculated. From this, in turn, (MnO), the concentration of the free MnO in the slag, can be got since :

$$(\text{MnO}) = \frac{(\text{FeO})[\text{Mn}]}{K_{\text{Mn}}},$$

where [Mn] is the concentration of manganese in the metal, and K_{Mn} is the true value of the manganese constant. The amounts of FeO and MnO combined as silicates are obtained by difference, and it is then possible, by trial, to evaluate the dissociation constants of the silicates.

The above forms the basis of the method used by H. Schenck and his co-workers to study the constitution of acid and basic furnace slags.^(168, 169) Starting with the former type of slag, they evaluated dissociation constants for the silicates, and then used the information thus obtained to elucidate the more complex constitution of the basic slag. Their conclusions differ somewhat from those described above ; for instance, they deduce that the orthosilicates of manganese and iron are the principal silicates occurring in acid slags. In basic slags they find evidence for the existence of calcium silicates (probably the metasilicate chiefly), calcium ferrites (of which the compound $\text{CaO.Fe}_3\text{O}_4$ is probably the most important), calcium phosphates (probably the tetrphosphate mainly) and manganese and iron orthosilicates. All of these compounds are partially dissociated, so that various amounts of the free oxides also occur. Their method is, however, somewhat "rough," in that they express all slag concentrations as weight percentages, whereas molar fractions are undoubtedly preferable, though adding very considerably to the labour involved in calculating the constants. To compensate for this they fall back in some cases on thermo-chemical criteria for confirmation.

An entirely different concept of slag constitution has been put forward by Herasymenko,⁽¹⁷⁰⁾ who believes that the slag compounds undergo complete dissociation of an ionic type in the liquid slag in the same manner as do most salts on melting.* McCance,⁽¹⁾ on the other hand, has suggested that the variations observed in the values of the slag-metal constants may be due mainly to changes in the activity coefficients of the reactants brought about by changes in slag composition. The methods described above depend on the assumption that such influences are of secondary importance only. In view of the magnitude of the composition changes involved, this would appear rather a considerable assumption to make, and its final justification will depend entirely on the extent to which methods of this kind can interpret the behaviour of the liquid slag.

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* As molten slags appear to have appreciable electrical conductivity it is probable that some dissociation of this type does occur.

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ADDENDUM TO PAPER.

In presenting the paper, Dr. WHITE said that since it had been written further information concerning some of the systems discussed had become available, and gave the following brief account of it.

The existence of merwinite is now established. A paper by Phemister⁽¹⁹⁶⁾ describing its occurrence in blast-furnace slags has been followed by another by Parker and Nurse⁽¹⁹⁷⁾ on its thermal and phase relationships in the system CaO-MgO-SiO_2 . It melts incongruently at 1590°C. , forming 2CaO.SiO_2 and a liquid.* It has also been identified in basic electric and open-hearth slags by Goldschmidt and Rait,⁽¹⁹⁸⁾ who have also prepared both it and its manganese analogue synthetically in unfused mixtures. Bowen and Schairer⁽¹⁹⁹⁾ have determined the equilibrium diagrams of the systems pseudo-wollastonite/akermanite and pseudo-wollastonite/diopside, both of which were found to be binary. There is no solubility of akermanite in either pseudo-wollastonite or wollastonite, and the supposed compound 5CaO.2MgO.6SiO_2 does not exist. There is, however, some solubility of diopside in wollastonite, which raises the temperature of the inversion to pseudo-wollastonite to 1368°C. , when 21% of diopside is present in solution. Errors arose in previous investigations, owing to the difficulty of quenching some of the melts to glass.

Fig 5(A) should, therefore, be modified by the deletion of the shaded area showing the α - and β -wollastonite solid-solution ranges, and by the insertion of two new invariant points on the 2CaO.SiO_2 -akermanite and the 2CaO.SiO_2 -MgO boundary curves at 1400°C. and 1580°C. , respectively, these being joined by the boundary curve between the 2CaO.SiO_2 and merwinite fields with a maximum at 1590°C. where it crosses the merwinite-monticellite join.* In Fig. 5(B) all the ties from 5CaO.2MgO.6SiO_2 should be eliminated and replaced by a single tie from wollastonite to diopside. Merwinite will occur in Fig 7(A) and manganese merwinite in Figs. 7(A) and 7(D). Corresponding changes are necessitated in Fig. 12(A).

The systems pseudo-wollastonite/diopside/anorthite and pseudo-wollastonite/akermanite/gehlenite have been studied by Osborn⁽²⁰⁰⁾ and by Osborn and Schairer,⁽¹⁷⁹⁾ respectively. Four such ternary planes in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ have now been studied, the other two being forsterite-anorthite- SiO_2 ⁽¹⁸²⁾ and $2\text{CaO.SiO}_2\text{-MgO-5CaO.3Al}_2\text{O}_3$.⁽²⁰¹⁾

There is now evidence that the tie $\text{MgO-CaO.Fe}_2\text{O}_3$ of Fig. 9(C)

* At the time of writing, a paper by Osborn on the stability relations of merwinite in the system CaO-MgO-SiO_2 has just appeared.⁽²⁰³⁾ The findings are similar to those of Parker and Nurse, though the boundary curves are displaced somewhat relatively to theirs. Thus, his CaO.SiO_2 -merwinite boundary does not cross the merwinite-monticellite join. It has, therefore, no maximum and slopes continuously towards the 2CaO.SiO_2 -merwinite-akermanite invariant point.

should be replaced by the tie $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ – $\text{MgO} \cdot \text{Fe}_2\text{O}_3$. (Dr. J. R. Rait, private communication.) This will necessitate a corresponding change in Fig. 20(*F*). The new phase distribution on the CaO – MgO – Fe_2O_3 face of the tetrahedron appears to be inconsistent with that shown on the CaO – Fe – Fe_2O_3 face. If, however, the latter is altered to conform with Fig. 19(*D*) instead of Fig. 19(*A*), it is possible to construct a quaternary diagram, though there are as yet insufficient data to distinguish between the various possibilities that arise.

A thermal equilibrium diagram for the system MnO – Al_2O_3 – SiO_2 has been published by Snow.⁽²⁰²⁾ In the stable system two ternary compounds occur, a cordierite analogue ($2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) and spessartite ($3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) which is apparently the first garnet found capable of co-existing with a liquid phase.

New papers on the system CaO – P_2O_5 – SiO_2 have been published by Barrett and McGaughey⁽²⁰³⁾ and by Trömel.⁽²⁰⁴⁾ Both confirm the binary nature of the join $2\text{CaO} \cdot \text{SiO}_2$ – $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and indicate extensive solid solubility between the phases occurring on it. According to Barrett and McGaughey these are four in number, α - $2\text{CaO} \cdot \text{SiO}_2$ (homogeneity range nil to about 21% $3\text{CaO} \cdot \text{P}_2\text{O}_5$), a silicophosphate (homogeneity range 26–51% $3\text{CaO} \cdot \text{P}_2\text{O}_5$), silicocarnotite (homogeneity range 66–77% $3\text{CaO} \cdot \text{P}_2\text{O}_5$) and α - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (homogeneity range 85–100% $3\text{CaO} \cdot \text{P}_2\text{O}_5$). The former silicophosphate they found to correspond with that isolated by Nagelschmidt⁽²⁰⁵⁾ from an open-hearth slag and having the approximate composition $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$ (47.1% $3\text{CaO} \cdot \text{P}_2\text{O}_5$). They, therefore, named it nagelschmidtite. Nagelschmidt had already shown by X-ray and optical examination that the phase that he had separated was identical with the silicophosphate $9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$ described by Körber and Trömel.⁽⁷⁰⁾ He states in his paper that Trömel later modified the latter formula to $8\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2.5\text{SiO}_2$. All three formulæ lie within the homogeneity range of nagelschmidtite as given by Barrett and McGaughey.

The ternary diagram given by Barrett and McGaughey differs from Fig. 14(*B*) in that the tie $4\text{CaO} \cdot \text{P}_2\text{O}_5$ –nagelschmidtite replaces the tie CaO –silicocarnotite, and the tie SiO_2 – $3\text{CaO} \cdot \text{P}_2\text{O}_5$ replaces the tie silicocarnotite– $2\text{CaO} \cdot \text{P}_2\text{O}_5$. The remaining ties are $3\text{CaO} \cdot 2\text{SiO}_2$ to nagelschmidtite, $\text{CaO} \cdot \text{SiO}_2$ to nagelschmidtite, to silicocarnotite and to $3\text{CaO} \cdot \text{P}_2\text{O}_5$, and SiO_2 to $2\text{CaO} \cdot \text{P}_2\text{O}_5$ and to $\text{CaO} \cdot \text{P}_2\text{O}_5$. The liquidus diagram given by these authors confirms that high melting points occur along the $2\text{CaO} \cdot \text{SiO}_2$ – $3\text{CaO} \cdot \text{P}_2\text{O}_5$ join and between this join and the CaO apex of the diagram. A ternary eutectic melting at 1600°C . is shown close to the composition of eutectic *E* of Fig. 14(*B*). On the other side of the $2\text{CaO} \cdot \text{SiO}_2$ – $3\text{CaO} \cdot \text{P}_2\text{O}_5$ join the melting points drop fairly rapidly with decreasing CaO .

According to Trömel the homogeneity ranges on the $2\text{CaO} \cdot \text{SiO}_2$ – $3\text{CaO} \cdot \text{P}_2\text{O}_5$ join are α - $2\text{CaO} \cdot \text{SiO}_2$ (nil to about 3% $3\text{CaO} \cdot \text{P}_2\text{O}_5$), a silicophosphate series *K* (8–20% $3\text{CaO} \cdot \text{P}_2\text{O}_5$ approximately),

a second very extensive silicophosphate series R (27–70% $3\text{CaO} \cdot \text{P}_2\text{O}_5$ approximately) and α - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (85–100% $3\text{CaO} \cdot \text{P}_2\text{O}_5$). The R series includes the compositions $9\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{SiO}_2$, $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$ and $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ (silicocarnotite). Silicocarnotite as a separate crystalline phase appears only at temperatures below $1300^\circ \text{C}.$, as a result of a peritectic reaction between the R and the α - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ phases. As a consequence, the homogeneity ranges of these two phases becomes appreciably restricted below $1300^\circ \text{C}.$, though they do not disappear from the diagram. At lower temperatures a still further reduction of the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ range should accompany the transformation to the β -form, as $2\text{CaO} \cdot \text{SiO}_2$ in solution is shown to lower the temperature of the α - β inversion markedly. These circumstances recall Kroll's statement (see Section VIII. of paper) that the hexagonal phase forming the "mother mass" of his slags tended to break down on slow cooling. In the ternary diagram only the portion of the liquidus surface lying within the area $\text{CaO}-2\text{CaO} \cdot \text{SiO}_2-3\text{CaO} \cdot \text{P}_2\text{O}_5$ is shown. A single eutectic trough runs from the $\text{CaO}-2\text{CaO} \cdot \text{SiO}_2$ eutectic to the $4\text{CaO} \cdot \text{P}_2\text{O}_5-3\text{CaO} \cdot \text{P}_2\text{O}_5$ eutectic. There are four reaction points on this trough, three arising from the peritectic reactions occurring between the phases on the $2\text{CaO} \cdot \text{SiO}_2-3\text{CaO} \cdot \text{P}_2\text{O}_5$ join, and the fourth from the peritectic dissociation of $4\text{CaO} \cdot \text{P}_2\text{O}_5$, which is now considered by Trömel to melt incongruently, instead of congruently as shown in his earlier diagram (Fig. 14(A)).

At present it is not possible to discriminate between the somewhat conflicting evidence supplied by the two papers, though Barrett and McGaughey's investigation appears to have been the more detailed. Their figure for the solubility of $3\text{CaO} \cdot \text{P}_2\text{O}_5$ in $2\text{CaO} \cdot \text{SiO}_2$ seems to be too high, however. Zerfoss and Davis⁽²⁰⁶⁾ have recently found that maximum lowering of the α - β inversion in $2\text{CaO} \cdot \text{SiO}_2$ is given by 1% of P_2O_5 in solution, this being apparently the limit of solubility. Trömel's paper also gives additional data on the range of liquid immiscibility in the system $\text{CaO}-\text{FeO}-\text{P}_2\text{O}_5$ described by Oelsen and Maetz⁽¹⁸⁶⁾ (see footnote on p. 672 p).

A series of determinations of the Fe_2O_3 contents of $\text{CaO}/\text{iron-oxide}/\text{SiO}_2$ melts in equilibrium with liquid iron at $1600^\circ \text{C}.$ has been made by Fетters and Chipman.⁽²⁰⁷⁾ Their data when recalculated give a series of curves running approximately parallel to those shown in Fig. 21(E). The main differences are (1) the Fe_2O_3 contents are in general somewhat lower than those indicated by Bowen, Schairer and Posnjak's data (which were obtained at a considerably lower temperature) but agree rather closely with the values calculated from Körber and Oelsen's data, and (2) the curves tend to converge as the $\text{CaO}-\text{SiO}_2$ edge of the diagram is approached, instead of diverging as the curves of Fig. 21(E) do.

An important paper by Mason⁽²⁰⁹⁾ on the phase relationships between the oxides of manganese and those of iron (the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{MnO}-\text{Mn}_2\text{O}_3$) has also appeared recently.

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DISCUSSION.

Dr. A. McCANCE, F.R.S. (Vice-President; Messrs. Colvilles, Ltd., Glasgow) : The author has done a very useful service as well as a tremendous amount of work in gathering together, in as compact a form as possible, all the known facts concerning the constitution of steelmaking slags, and his paper will be a valuable source of reference. The accumulation of knowledge and the large number of compounds which are already known to exist in such slags make the need for a connecting theory to correlate the facts very evident, and it is to be hoped that this aspect of the subject will soon be tackled vigorously.

While the constitution in the solid state, as the author has shown, must necessarily dominate our point of view in the present developing stage, the constitution of slags in the liquid state might be very different. Slags are essentially solutions, and our difficulty at the present time is to know what compounds act as solvents and what compounds act as solutes. Is a basic slag a solution of FeO in $2\text{CaO} \cdot \text{SiO}_2$ or a solution of FeO in $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ or both, and, if both, do the solvents share the available FeO in proportion or does one become dominant over the other?

These are the questions we should like the author to examine and decide. It can only be done from the experimental side, as there is an insufficient theoretical basis to supply the answers. The experiments made by the author on the dissociation pressure of ferric oxide point to a possible way by which this question might be examined, and, in this connection, I do not think one can escape

the application of the concept of activity to slag solutions. It is very probable that the mass-action effect of many compounds is very different from their molecular proportion. The dissociation pressure is directly connected with the activity, and if the variation in the dissociation pressure of calcium ferrite with added FeO were measured a beginning to the required answer might be forthcoming. The author has already carried out a number of experiments along this line, but there are still missing links before the settlement of this question is possible.

I do think that the activity concept is the most fruitful when studying the constitution of slags, and the work which has already been carried out on ionic solutions in water has placed this idea on a sound theoretical basis. There is, consequently, no longer any need to hesitate in the development of the idea in other directions.

The constancy of the sum of $\text{CaO} + \text{MnO} + \text{FeO}$ in acid slags which the author has examined in great detail, while useful to some extent, has little theoretical significance and too much stress should not be placed on it. It arises from the fact that at 1600°C . the percentage of these oxides, which are in equilibrium with silica, is roughly as follows :

CaO	35%
MnO	50%
FeO	50%

In a mixture containing only manganese and ferrous oxides, the sum should be very constant. In the presence of lime, however, it will only be approximately constant, and the need for adjustment as the lime content increases arises from the lower content of lime in equilibrium with silica at this temperature. The result, therefore, while of practical importance, does not require any changes in our present theoretical knowledge.

A considerable amount of work, much of which is due to the author himself, has been carried out on the iron-oxygen diagram. While it is generally considered that the present diagram is not far removed from what can be accepted as final, I have always been a little doubtful about the horizontal line shown at 570°C . and the correctness of the eutectoid point shown in the neighbourhood of 24% oxygen. The 570°C . line is supposed to represent the breakdown of ferrous oxide into iron and magnetite, and, while this certainly takes place in the presence of carbon monoxide or hydrogen, I question whether this reaction would take place in the absence of small quantities of gases. I rather think that the vertical lines enclosing the wüstite area should be continued straight down and should indicate, in accordance with theory, the solubility limits of the adjacent phases. It would be well worth while carrying out the experiments with pure materials in a vacuum, so as to avoid the interfering effect of gases, and to find then whether the decomposition line, which is always accepted in the diagram, would persist.

In considering possible theories for the constitution of liquid

slags, I do not think that much consideration need be given to the ionic theory put forward by Herasymenko. Conductivity without ionic dissociation is already well known, and there has never been any demonstration of the transport of ions under the influence of an electric current with slags. This is an essential accompaniment of the ionic type of conductivity which is decisive, and no evidence has ever been put forward to show that it takes place. In the circumstances, therefore, one must conclude that the conductivity of liquid slags is of the electronic type and similar to the conductivity of large numbers of the materials which are insulators at low temperatures but conduct when sufficiently heated.

Dr. A. F. HALLIMOND (Geological Survey and Museum, London) : During the last war my notes for slag research included about two dozen references of the kind dealt with in the present paper. They were mainly from the Washington Geophysical Laboratory; now, the publications list of that institution alone has well exceeded 1000, and there are many other active research bodies. The present paper is therefore a most welcome guide to this important material, and I am sure it will be constantly in the hands of those engaged in this class of work.

The author necessarily omits detailed mineralogical descriptions. These are of great importance in the practical use of the phase-rule data, since the rapid examination of a microscope slide can often supplement or replace costly methods of separation and analysis. I personally have the impression that more might have been done on this side in recent years, especially in the study of material crystallised from melts of commercial composition as well as that from ideal simple mixtures.

It used to be a device of some reviewers to indicate a few misprints, presumably as evidence that they had read the work in question. I hope no one will think that I am claiming to have given adequate consideration to the present paper in the short time available, if I mention a detail that I notice on p. 597 P. The author refers to "vogtite, since shown to be isomorphous with wollastonite." It would be a more precise statement of the facts if this expression was reversed, for the slag mineral vogtite was named by Hlawatsch in 1907 and has undoubted priority over the later discovery that a mineral which had been classed as wollastonite was really a naturally occurring form isomorphous with vogtite. The fact is that Bowen, in 1933, pointed out that vogtite and wollastonite had close crystallographic similarity though belonging to different systems; Peacock, in 1935, confirmed that the majority of specimens described as wollastonite were not in fact identical with that well-known monoclinic mineral from Vesuvius, but were triclinic and apparently isomorphous with vogtite, which had been known in slags for many years. Natural vogtite contains notably less iron than the slag mineral, and is so like wollastonite that it would have been per-

missible to call it parawollastonite. At this point, however, Peacock discarded the ethics of priority and made the reverse proposal that the well-known Vesuvian mineral should (in future) be called "parawollastonite" and the natural vogtite "wollastonite," on the plea that the former seems to be rare. As often happens when priority is disregarded, there may be great confusion in reading the earlier literature, for it is only if we accept this terminological "sleight-of-hand" that vogtite can be said to be "isomorphous with wollastonite."

Dr. G. R. RIGBY (The British Refractories Research Association, Stoke-on-Trent): This report on open-hearth slags is useful from several angles. First, almost all the relevant knowledge concerning slag systems has been collected together. It is true that since the paper was written several more equilibrium diagrams have been published, and I hope that Dr. White will be in a position to keep his report up-to-date by giving us periodical reviews of the literature. Secondly, Dr. White's paper makes it obvious where the gaps in our knowledge lie. Everyone who reads the paper soon realises that our information regarding ternary systems containing MnO as a constituent is much less than that on the corresponding systems containing FeO. Those of us who are interested in refractory materials are seriously impeded by the meagre data on equilibrium diagrams containing Cr_2O_3 . A start has, however, been made, and the $\text{MgO}-\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$ diagram has recently been published by W. T. Wilde and W. J. Rees.¹

The paper, however, is much more than a mere collection of data; the great value of Dr. White's work lies in the interpretation of such data, particularly with reference to the composition of slags.

As an example we might consider the author's discussion on the Ca-Fe-O ternary system. Here it is pointed out that the action of ferrous oxide on lime is quite different from its action on magnesia, a point of great interest in connection with basic hearths. MgO and FeO form a complete series of solid solutions; in the presence of CaO, however, FeO is unstable and dissociates into Fe_2O_3 and metallic iron. Thus the action of FeO slags on lime results in the formation of metallic iron and dicalcium ferrite, provided that the temperature is such that this latter compound is not extensively dissociated. I have recently examined petrologically a piece of a used dolomite hearth. Thin sections cut at various positions below the surface show that in the first 4 in. of the hearth ferrous oxide has been absorbed entirely by the periclase crystals, the lime remaining unaffected except where it has combined with silica to give $3\text{CaO}.\text{SiO}_2$. It is not until positions lower than 4 in. below the surface are reached that dicalcium ferrite can be detected, presumably because the temperatures of the hearth above this region were too high for dicalcium ferrite to remain stable.

¹ *Transactions of the British Ceramic Society*, 1943, vol. 42, July, p. 123.

I would also like to comment on the section concerning the oxygen pressures of various iron compounds. At the Mellor Laboratories we have been preparing a number of synthetic iron minerals and noting their rates of reduction in a current of hydrogen. We have found that whereas Fe_2O_3 and $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ are comparatively easily reduced, fayalite and hercynite are reduced with much more difficulty, and the order of increasing resistance to reduction is the same as that given by Schenck and reported on p. 627 P of the paper. I should, however, like to draw attention to the oxygen pressures of Fe_2O_3 - Cr_2O_3 solid solutions as measured by N. G. Schmahl.¹ He found that such solid solutions had a much lower oxygen pressure than those of the Fe_2O_3 - Al_2O_3 series. We have also found, in confirmation of this, that chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, is even more difficult to reduce in a current of hydrogen than is hercynite.

Finally, may I say a few words about the constitution of acid open-hearth slags. I have examined only a very limited number of such slags in thin section under the microscope, but in none of those studied have I ever seen fayalite as a constituent. On the other hand, all the slags have contained the products of dissociation of fayalite—wüstite and cristobalite. Puddling slags which I have examined have invariably contained fayalite as a major constituent. I have previously explained these observations by assuming that at the higher temperatures of the acid open-hearth furnace fayalite is unstable and is highly dissociated into FeO and SiO_2 . I should be interested to learn whether Dr. White supports this inference. Only a day or so ago we were preparing a solid solution consisting of equimolecular proportions of $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$ and $\text{MgO} \cdot \text{FeO} \cdot \text{SiO}_2$. As we did not know the exact melting point of such a mix we fused the materials at a temperature about 30°C . higher than the melting point. An examination of the slowly cooled material showed that slight decomposition had occurred with the deposition of wüstite. All these melts were made in an atmosphere of nitrogen. The dissociation of fayalite is of great importance in connection with the reactions which occur between metal and slag, as set out by Schenck, mentioned on p. 688 P of the paper.

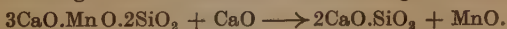
Dr. J. R. RAIT (Messrs. William Jessop & Sons, Ltd., Sheffield) : Much attention has been paid to the reactions between slag and metal, but more recently attention has also been focused on the reactions between slag and refractory and liquid steel and refractory. Dr. White has illustrated by means of the FeO - Al_2O_3 - SiO_2 system the very drastic fluxing action of FeO on silica refractories containing small amounts of alumina. This is particularly interesting in acid open-hearth bottoms. Since pure sand is too refractory, some loam (alumino-silicate) is mixed with it to facilitate fritting. However, unless the amount of loam is limited, the resulting alumina content will be too high and the hearth will be subject to

¹ *Zeitschrift für Elektrochemie*, 1941, vol. 47, Dec., p. 835.

severe corrosion by FeO, resulting in loss of output and dirty steel.

The author has shown that with increasing MgO content of basic open-hearth slag, the saturation content of lime decreases, so that the amount of dephosphorisation decreases. Accordingly, the author has suggested that dephosphorisation will be less effectively carried out in a magnesite hearth and that dolomite hearths are to be preferred in basic open-hearth furnaces from the dephosphorisation point of view. On the other hand, magnesite may be superior to dolomite in basic electric-furnace practice. During the oxidising stage some of the P_2O_5 combines with the lime of the dolomite to form a calcium phosphate, and during the reducing stage of the process some of this phosphate in the hearth is reduced, resulting in a pick-up of phosphorus in the metal. The amount of phosphate formed in a magnesite hearth should be less than in a dolomite hearth during the oxidising stage.

The author's system of phase assemblages is an excellent attempt to systematise the constitution of slags, but it will require considerable modification, because the data on which it is based are not met entirely satisfactorily. For example, the tie-lines in the $CaO-MgO-Fe_2O_3$ system should be $2CaO.Fe_2O_3-MgO$ and $2CaO.Fe_2O_3-MgO.Fe_2O_3$.¹ Accordingly the phase groupings in the more complicated systems containing CaO, MgO and Fe_2O_3 are unsatisfactory. In addition, merwinite and its analogues will frequently be constituents of basic slags. Recently the existence of the manganese analogues of merwinite with the molecular formula $3CaO.MnO.2SiO_2$ was reported.² This compound has a type of lattice similar to that of merwinite with a slightly different spacing and will be isomorphous with $3CaO.MgO.2SiO_2$. Manganese merwinite may be of great interest in basic open-hearth melting. For example, if this compound exists in the liquid slag the addition of lime to the slag would remove it according to the equation:



The MnO set free would be partly reduced by metallic iron, causing a return of manganese to the metal. I should like to ask the basic open-hearth melters whether manganese does return to the metal on the addition of lime to slags with high silica contents.

Dr. J. H. CHESTERS (The United Steel Companies, Ltd., Stocksbridge, near Sheffield): I should like to ask two questions, which concern us immediately and practically. The first is this: If a large sample of basic slag—for example, a sphere 5 ft. across—were cooled by allowing it to radiate to the atmosphere, so that it cooled in anything from 12 to 24 hr., would the author expect there to be marked segregation? That is to say, would he expect a different chemical composition inside from that which would be found nearest

¹ J. R. Rait, unpublished work.

² H. J. Goldschmidt and J. R. Rait, *Nature*, 1943, vol. 152, p. 356.

the shell, and, if so, what sort of laws would control such segregation? The other question is this: Taking a typical basic slag—and I have in mind particularly a high-phosphoric slag—what is likely to be the effect of adding alumina in amounts of up to 5%? Would one expect a drop or a rise in either the melting point or the viscosity?

Mr. J. H. WHITELEY (The Consett Iron Co., Ltd., Consett, Co. Durham): To my mind this is a valuable paper and I have no criticism to make of any kind. There are one or two things, however, which I might mention in connection with the subject. As Dr. McCance has indicated, it is a moot point as to how far the identification of the mineral constituents of solid slags can assist the processes of steel manufacture. The efficiency of the liquid slag in the furnace seems to depend upon three things, *viz.*, the viscosity, the oxidising power of the metallic oxides and the retentivity of the slag in basic practice for phosphoric acid and sulphur. Now, it is a remarkable fact that, in making mild steel by the acid process, the bath will sometimes go completely off the boil when the carbon in the steel is about 0.25%. Usually, in such cases, the charge has been overfed with ore, so that the slag is in an open condition and contains 32% of FeO or more. Normally in good practice the boil will continue until the carbon has dropped to about 0.15%, and the only way I know of rectifying the stagnant state when it arises is to take both the gas and air off for several minutes so as to cool the bath. Now, the slags which give rise to this effect do not as a rule contain lime, the only bases present in any quantity being FeO and MnO, and, as Dr. White has indicated, a melt of these substances with SiO₂ can form two immiscible solutions at about 1690° C. That temperature is probably 50° C. higher than that of a stagnant bath, and I would ask Dr. White whether he thinks that a small range of immiscibility could appear at a temperature well below 1690° C. Even so, of course, the solution rich in SiO₂ should rise to the surface, since it is the lighter one, but I am not greatly perturbed about that, for so many things happen in a steelworks which are not in accordance with expectation.

There is also the question as to what bearing the constitution of a slag has on foaming. I would mention an instance which occurs in an acid furnace. When the silicon content of the charge is well over 1.0%, the heavy additions of ore required to bring the bath to the boil invariably cause the slag to stand up, as the furnacemen say. In other words, it foams. Now, during that period the silicon is being oxidised and the small globules of silica thus formed in the metal are rising into the slag. If these particles are not dissolved very quickly their presence might induce foaming. It is certainly the case that the slag settles down when the bath comes to the boil and that very few silica particles then remain in the metal. I would like Dr. White's opinion on this matter.

(Contributed later in writing). There are two further questions

that I would ask Dr. White in connection with slag formation and constitution. The first concerns the action of alumina in acid slags. As far as my experience goes, an alumina content of 3-4% seems to be amphoteric in its behaviour, in that it tends to open thick slags and close thin ones. In my opinion, the effect of alumina additions to acid slags has not received sufficient attention, and I would much appreciate any information that Dr. White can give on the matter. The other question relates to the use of fluorspar as a flux in basic practice. Can Dr. White say why it is that the addition of relatively small quantities of that mineral so readily causes an excess of lime to pass into solution?

AUTHOR'S REPLY.

Dr. WHITE replied: I should first like to express my thanks to all who have taken part in the discussion.

In reply to Dr. McCance, I agree that one of the primary needs now from the steelmaking point of view is for greater knowledge of the chemistry of the liquid slag. The apparent parallelism between the constitutional relationships in solid slags and the chemical properties of liquid slags is at best only qualitative and cannot yield quantitative information on slag-metal relationships. In some cases solid slag relationships may even be misleading. For example, the recent diagrams published by Barrett and McGaughey⁽²⁰³⁾ and by Trömel⁽²⁰⁴⁾ for the system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ both show a tie-line joining the phases $3\text{CaO.P}_2\text{O}_5$ and SiO_2 , indicating that these phases are stable in contact with one another in all proportions. Nevertheless, liquid slags high in silica lying on this join would be incapable of retaining phosphorus in the presence of the metal bath.

However, I do not think that we should underestimate the practical importance of the thermal equilibrium diagrams from the point of view of other aspects of the steelmaking process. Thus, they yield quantitative data on fusibility-composition relationships in furnace slags, on the slag-refractory reactions and on the factors governing the formation and elimination of non-metallic inclusions. They are also of primary importance to those who are concerned with the possible utilisation of slags—*e.g.*, for agricultural purposes.

I do not think there can be any disputing the usefulness of the activity concept in the study of liquid slags, but I feel that some confusion may be arising owing to there being two somewhat different uses of the terms "activity" and "activity coefficient." For instance, when silica is added to liquid ferrous oxide, the activity of the iron oxide is decreased to a greater extent than can be accounted for by mere dilution, and we can say that the activity coefficient of the *total* iron oxide content has decreased in the

presence of silica. That is one usage, and is, I think, the one adopted by Dr. McCance, as it is the more useful of the two from the thermodynamic standpoint. On the other hand, we may seek to account for the drop in the activity coefficient of the total iron oxide by evaluating a dissociation constant for a supposed ferrous silicate in the slag and speak of the activity of a supposed "free" FeO content. We might then find that the activity coefficient of this free FeO was the same as that of the FeO in the 100% ferrous-oxide slag, or we might have to introduce a variable activity coefficient to preserve the constancy of our dissociation constant with varying SiO_2 content. It is in this latter sense that I have used the terms "activity" and "activity coefficient" in the present paper, and also in an earlier paper on the constitution of liquid slags.⁽⁸⁴⁾ In the latter I found that the data on slag-oxygen and slag-metal equilibrium which I examined could be accounted for, approximately at least, by assuming the existence in the liquid slag of certain partially dissociated compounds, the activities of these and of the free oxides being taken as proportional simply to their molar fractions. It need hardly be pointed out that the conclusions reached were tentative only. Both usages are, however, permissible, and examples of both are to be found in the chemical literature. It is true that there is some doubt as to the actual existence in solution of such undissociated molecules (it has been suggested that they may have a transient existence, or, alternatively, that there may be simply a general attraction between the components into which the molecule has dissociated), but it may be noted that in the somewhat analogous case of ionic dissociation in aqueous solution, physical chemists still find it convenient and justifiable to evaluate dissociation constants, with the implied assumption of a proportion of undissociated molecules in solution. They do this even when they have to attribute variable activity coefficients to the supposed free-ion concentrations. They have the advantage, of course, that they have at their disposal expressions such as that of Debye and Hückel from which to calculate what the activity coefficients should be. Again, Chipman, who has been determining the activity of iron oxide in slags of various compositions, has, in a recent paper,⁽²¹⁰⁾ been seeking to account for the observed variation in the activity in terms of compound formation in the slag.

I am not certain that the possibility of ionic dissociation in slags can be dismissed altogether. As far as my own attempt to throw light on the constitution of liquid slags is concerned, I believe that the data could also be accounted for on the basis of an ionic type of dissociation. I should also like to point out that Martin and Derge⁽²¹¹⁾ have recently shown that liquid $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags have relatively high conductivities and can also be electrolysed. They conclude that ionic dissociation takes place in these slags to a considerable extent.

No fresh theoretical significance is, of course, implied in my

discussion of the relationships shown in Fig. 22 (*A*). I have simply tried to demonstrate within the quaternary system the relationships which Dr. McCance deduces from a consideration of the binary systems. The equations of the mean planes were given because they probably correspond approximately to those of the surface of saturation with silica at steelmaking temperatures, so that they should afford a means of estimating approximately the maximum possible silica content that any slag can carry.

The view that wüstite dissociates into Fe_3O_4 and metallic iron on cooling below 575°C . is supported by a considerable body of evidence provided by X-ray, microscopic and magnetic studies, and by studies of equilibrium in the systems Fe-O-C and Fe-O-H (*i.e.*, in the systems formed by iron and its oxides and gaseous mixtures of CO and CO_2 and of H_2 and H_2O , respectively). These last-mentioned investigations alone would seem to constitute a valid proof that such a breakdown must occur, as they show that below 575°C . the reduction of Fe_3O_4 proceeds directly to iron without the intervention of FeO . Further, the results show that below 575°C . the Fe_3O_4 - Fe equilibrium corresponds to a lower oxygen pressure than would the FeO-Fe equilibrium.

In reply to Dr. Hallimond, I agree with him as to the importance of the mineralogical descriptions of the minerals occurring in slags, but I feel that such descriptions would be best compiled by an expert petrologist, which I am afraid I cannot claim to be. I thank Dr. Hallimond for his extremely interesting account of the somewhat involved history of the wollastonites.

The case of the dolomite hearth described by Dr. Rigby is of considerable interest. According to Fig. 20 (*F*) the pick-up of iron oxide (assumed to be not all Fe_2O_3) would give first the phase grouping CaO , MgO , $2\text{CaO.Fe}_2\text{O}_3$ and Fe , followed, at higher iron-oxide contents, by the phase grouping MgO-FeO solid solutions, $2\text{CaO.Fe}_2\text{O}_3$ and Fe . No thermal equilibrium diagram is, of course, available, but it would appear that, corresponding to the first grouping, we should have at steelmaking temperatures a liquid containing all the iron oxide co-existing with CaO and MgO with which it would be saturated, and, corresponding to the second grouping, a liquid co-existing with the MgO-FeO solid-solution phase. The Fe_2O_3 content of the liquid phase would depend on the temperature and oxygen pressure. In the limit, in the presence of metallic iron, its composition would lie somewhat to the oxygen-rich side of a plane through CaO , MgO and FeO . In equilibrium with air it would lie somewhat further from this plane. However, on freezing, this liquid, whether in contact with metallic iron or air, would be bound to deposit some $2\text{CaO.Fe}_2\text{O}_3$ together with metallic iron. Hence the diagram as it stands does not explain Dr. Rigby's observations. Two suggestions may, however, be made: First, the absence of $2\text{CaO.Fe}_2\text{O}_3$ from the neighbourhood of the working surface may have been due to drainage from a higher- to a lower-

temperature zone such as often occurs when fluxes are picked up by refractories; and secondly, as regards the occurrence of CaO with MgO-FeO, this might be due to the fact that equilibrium had not been attained, or, alternatively, it may be an indication that, as I have suggested in Section VI. (f), a certain range of MgO-FeO solid solutions may be stable in contact with CaO. Actually, from the latter point of view, Dr. Rigby's results might quite well be construed as refuting the view that the tie $2\text{CaO}.\text{Fe}_2\text{O}_3\text{-Fe}$ occurs in this system.

Systems containing Cr_2O_3 were not considered in the present paper, as it was decided to restrict its scope to the slag constituents encountered in normal practice. There can be no gainsaying their importance, however, and the work being done at the Mellor Laboratories as well as the recent paper by Wilde and Rees are valuable contributions to our knowledge in the fields both of slags and of refractories. There are still many gaps to be filled, however, as Dr. Rigby has pointed out. For example, the behaviour of natural chromite at high temperatures in the presence of MgO or of iron oxide will only be completely understood when the oxygen-pressure/temperature/composition relationships in the appropriate systems have been worked out. In the iron-oxygen system, for instance, Fe_2O_3 and the spinel Fe_3O_4 are in equilibrium at 1388°C . at the oxygen pressure of the air. In the presence of other spinel-forming oxides, however, the phases concerned in this equilibrium are in general a "mixed" spinel and a sesquioxide solid solution, and equilibrium is now possible over a range of temperature. Further, this temperature range is raised above 1388°C . by some oxides and lowered by others. Thus, Al_2O_3 raises it, while MgO lowers it. Cr_2O_3 probably raises it, as the system Fe-Cr-O is probably rather similar to the system Fe-Al-O in its general relationships. These effects can be illustrated for the case of the system Fe-Al-O by reference to Fig. 20 (E). Imagine, for this purpose, a horizontal plane representing a constant oxygen pressure placed above the solid model depicted in that diagram. As the temperature is raised, the effect will be to raise the surfaces representing the dissociation pressure towards this plane. (The rate of rise with temperature will not in general be the same for all phases, but for the purposes of a qualitative discussion this need not worry us.) Those parts of the pressure surface which are highest will reach the plane first, and dissociation of the corresponding compositions will then proceed till the dissociation pressure of the resulting phase or phases is equal to that represented by the plane. It will readily be seen that $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixtures will require higher temperatures to cause them to dissociate than will Fe_2O_3 alone. I may say that a certain amount of work along these lines was carried out at the Royal Technical College, Glasgow, a few years ago, but did not pass beyond the exploratory stage, as the outbreak of war intervened.

I am rather surprised at Dr. Rigby finding wüstite and cristo-

balite co-existing in acid open-hearth slags. True, my own attempts to elucidate the molecular constitution of liquid slags indicated apparently that fayalite was completely dissociated in the liquid slag in favour of a metasilicate molecule and free FeO, but I have always regarded this conclusion as highly tentative. In any case I have never had any reason to expect that evidence of the constitution of the liquid slag might be preserved in the solid state. Acid slags may be an exception to this, however, as they are of high viscosity and tend to supercool to glasses from which crystalline phases separate by a process of devitrification. All I can say at the moment is that his finding is at least not incompatible with my own conclusions on the constitution of liquid silicate slags, for, though the dissociation was apparently into FeO and a metasilicate molecule in the liquid state, the latter would in turn become unstable in the solid state, as no metasilicate occurs in the solid system FeO-SiO₂.

With regard to the separation of wüstite from a CaO.FeO.SiO₂-MgO.FeO.SiO₂ mixture heated to above its melting point, I feel that some caution in interpretation is necessary. For example, incongruent melting of the resultant phase (I imagine one phase might result from such a mixture) might account for the occurrence of wüstite.

I have already referred to Dr. Rait's finding that the tie 2CaO.Fe₂O₃-MgO.Fe₂O₃ occurs in the system CaO-MgO-Fe₂O₃ (see Addendum) and to his discovery, with Mr. Goldschmidt, of manganese merwinite. His further remarks illustrate how a knowledge of the thermal equilibrium diagrams can be of use in tackling one aspect at least of steelmaking, *viz.*, the problem of the reaction between slag and refractory. His other reference to the reactions that may occur between liquid steel and refractories is, I think, particularly apposite at the present time. Hitherto, the makers and users of refractories have not worried much about this particular aspect, but its importance will probably become increasingly realised. Dr. Rait himself has shown⁽²¹²⁾ that free silica in casting-pit refractories is liable to be reduced by steel containing manganese, and that the trouble can be largely overcome by the use of firebrick of higher alumina content. Dr. McCance had earlier discussed this question from the theoretical standpoint.⁽¹⁾ Another refractory material readily reduced by powerful deoxidisers is chromite, which may lead to rapid attack with accompanying pick-up of chromium by the metal. For certain uses the application of thermodynamic criteria to the choice of refractory may save a considerable amount of trouble.

In reply to Dr. Chesters, it is quite possible that slow cooling of a relatively large mass of basic slag may result in a certain amount of segregation, in view of the facts that most basic slags should have a relatively long freezing range and that the residual liquid is liable to be very fluid. Instances of segregation have been given by

Hilgenstock,⁽¹³⁹⁾ while Schneiderhöhn⁽⁷⁷⁾ has given details of structures produced from a given slag by different rates of cooling. The latter also states that different constituents may crystallise from slags of substantially similar composition under different conditions of freezing. According to Trömel,⁽²⁰⁴⁾ segregation results from the fact that there is a tendency for an iron- and manganese-oxide-rich phase to separate as a distinct layer in liquid slags. This he attributes to the existence of a range of liquid immiscibility in the system $\text{CaO-FeO-P}_2\text{O}_5$ as established by Oelsen and Maetz⁽¹⁸⁶⁾ and later by himself. He also claims that quick cooling tends to prevent the formation of silicocarnotite, which, according to his finding, is formed only below 1300°C . and by reaction between solid phases.

The addition of Al_2O_3 to a slag high in CaO , without alteration of the other constituents, should in general cause a lowering of the fusion temperature. If, however, Dr. Chesters is concerned with the comparison of two slags of substantially the same analysis except that in one the Al_2O_3 content has been raised at the expense of the other acid oxides, the answer is that Al_2O_3 appears to cause relatively little difference in amounts of a few per cent. at least. The effect of Al_2O_3 on the fluidity of a number of industrial basic slags was studied by Hartmann.⁽²¹³⁾ According to his observations, Al_2O_3 additions of up to 10% of the weight of the slag had little effect on the fluidity, unless the Al_2O_3 was added as bauxite containing appreciable iron oxide, when there was a rise in fluidity due to the increased iron-oxide content of the slag.

The first point raised by Mr. Whiteley as to the usefulness of the thermal equilibrium diagrams to the steelmaker has, I think, been dealt with in my replies to previous speakers. With regard to his second point, the temperature of immiscible-liquid formation can be appreciably lower than 1690°C . in slags of certain composition; for instance, iron-oxide/silica slags high in silica heated in equilibrium with the oxygen of the air melt completely to give immiscible liquids at 1665°C . on the Geophysical Temperature Scale (see Fig. 18 (*F*)). The lowest temperatures that I have seen recorded for immiscible-liquid formation are those by Barrett and McGaughey for the system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ ⁽²⁰³⁾ and by Flint and Wells for the system $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$.⁽²¹⁴⁾ In these systems immiscible liquids are formed at temperatures as low as 1400°C . and 965°C ., respectively. The particular slags in which this occurs, however, are high in P_2O_5 and B_2O_3 , respectively, so they can be ruled out from the present discussion. Actually, it might not be necessary to invoke the aid of liquid silica to explain the phenomenon that Mr. Whiteley describes, as the same conditions which would cause the separation of immiscible liquid silica from an acid slag at a high enough temperature would cause the separation of solid silica at a lower temperature. This might occur at the slag-metal interface if very rapid reduction of the iron oxide occurred, and might be aggravated if rapid elimination of silicon from the bath were occurring at that time. It is difficult to see, however,

how any such condition could be remedied by cooling the furnace. Personally, I should be inclined to look for the cause first of all in the nature of the slag-metal equilibrium relationships. For example, if under the conditions described it was found that the carbon had dropped too fast relative to the silicon and manganese, this could account for the bath going off the boil. According to the most recent data quoted by Chipman,⁽²¹⁰⁾ the equilibrium $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$ is displaced to the right by falling temperature, which might explain why lowering the temperature brought back the boil. Whether or not this was the case could, I think, be established by a study of the metalloid-elimination curves for such heats.

The cause of frothing in slags has not yet, as far as I am aware, been elucidated. Generally, the conditions favourable for froth formation are encountered when a liquid of relatively high surface tension has dissolved in it a solute that lowers the surface tension appreciably. Such a solute is then preferentially adsorbed at any free surfaces of the liquid (as indicated by the well-known equation of Gibbs), and if gas bubbles are produced by passing gas through the liquid, or by the evolution of gas within the liquid, a stable froth is produced. The necessary condition for silica in solution, or silica particles in suspension, to favour froth formation would then be that, by concentrating at the bubble surfaces, it, or they, should effect a diminution in the surface energy. At present it is hardly possible to make a pronouncement on this point for lack of data, though a certain amount of work on the surface tension of molten glass has been carried out by Badger, Parmelee and Williams.⁽²¹⁵⁾ These authors determined the effect of various additions on the surface tension of a soda-alumina-silica glass and found that Al_2O_3 , iron oxide, manganese oxide and lime additions all raised the surface tension appreciably. So also did silica, but to a less marked degree. I do not know whether one would be justified in deducing from this that in, say, a FeO-MnO-SiO_2 slag the addition of FeO and MnO would raise the surface tension while silica would lower it. Actually, I think that most people who have observed the appearance of silicate slags melted in metal crucibles would be inclined to believe that the reverse was the case, though I do not know that this would be justified either, as the interfacial tension between slag and metal is involved in such cases, while the influence of viscosity, which increases rapidly with increasing SiO_2 , may be misleading.

There is little doubt, however, that surface-tension effects can be exceedingly important in slags. Preston and Turnbull,⁽²¹⁶⁾ for instance, have recently shown that surface-tension effects are mainly responsible for the "upward drilling" of glass tank refractories by molten glass. Incidentally, if Mr. Whiteley's conception of a slag containing numerous particles of undissolved SiO_2 in suspension is correct, it might be possible to account for frothing even if it were found that SiO_2 raised the surface tension of the slag, for in that case the SiO_2 particles would automatically repel all gas

bubbles coming in contact with them and might seriously obstruct the escape of such bubbles to the surface.

The effect of Al_2O_3 on acid slags is of considerable theoretical interest. From the thermal equilibrium diagrams for the basic-oxide- Al_2O_3 - SiO_2 systems it will be seen that a small content of Al_2O_3 causes the complete elimination of the range of liquid immiscibility and brings the liquidus surface of saturation with SiO_2 close to the composition of SiO_2 at steelmaking temperatures. Such SiO_2 contents are, of course, never encountered in steelmaking, presumably because the viscosities of such high-silica slags are much too high. As far as the effect of Al_2O_3 itself on the viscosity of acid slags is concerned there is a decided scarcity of data, but, if the available data on the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ can be taken as a guide, it appears that Al_2O_3 itself causes a progressive rise in viscosity, particularly when the SiO_2 content is high. One might, therefore, venture tentatively to explain Mr. Whiteley's observations on the "amphoteric" nature of Al_2O_3 as follows: If a slag is too viscous, owing to its being supersaturated with SiO_2 , Al_2O_3 would probably decrease its viscosity by increasing its capacity to dissolve SiO_2 . If, on the other hand, the slag were fluid, owing to a deficiency of SiO_2 , Al_2O_3 might thicken it by virtue of its own effect on the viscosity.

Fluorspar appears to act as a flux for CaO by virtue of the fact that it forms a low-melting eutectic with it. According to Körber and Oelsen,⁽¹⁷⁸⁾ a eutectic melting at under 1400°C , with 80% of CaF_2 and 20% of CaO is formed. The liquidus curve, therefore, drops very steeply from the melting point of lime to this eutectic, and a similar effect is, I think, to be expected in more complex basic slags. In addition to this, fluorspar has a very marked effect on slag fluidity which I do not think has been fully explained yet. I believe it has been suggested that it may be due to the presence of highly mobile fluorine ions or simply of fluorine gas dissolved in the slag. It is known that the presence of dissolved gases in some glasses can produce a considerable lowering of the viscosity.

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A REVIEW OF BASIC OPEN-HEARTH PRACTICE AT AN AUSTRALIAN PLANT.

By R. L. KNIGHT (AUSTRALIAN IRON AND STEEL, LTD., PORT KEMBLA, N.S.W., AUSTRALIA).

This paper was discussed at the Annual General Meeting held in London on May 13, 1943; in the author's absence it was presented by Mr. A. Robinson. It will be found, together with the discussion and correspondence to which it gave rise, in the *Journal of The Iron and Steel Institute*, 1943, No. I., p. 233 P. The author's reply was not received in time for inclusion with the paper itself, and is printed below.

AUTHOR'S REPLY.

Mr. KNIGHT wrote in reply: With reference to Dr. Gregory's comments, sand is used for three main reasons:

- (1) To inhibit the rise of FeO in the slag.
- (2) To replace fluorspar and bauxite as a flux and break up the lime on all grades except rimming heats.
- (3) To promote manganese reversion to the bath and thus economise in ferro-alloy consumption.

It is agreed that manganese oxide does play an important part in the slag reactions. The precise mechanism of these reactions is debatable, but it is significant that the use of sand is abortive below an approximate bath carbon content of 0.3%.

A sand addition is invariably followed by a reduction in the bath carbon, and it therefore appears that the primary function of sand is as stated.

The oxidising power of the slag and the concentration of manganese in it govern the movement of manganese from the slag to the bath and *vice versa*.

The methods employed for rapid determinations on the open-hearth floor are:

Silica.

Take 0.5 g. of finely ground sample, place in a 400-c.c. beaker, add 5 c.c. of hot water plus 5 c.c. of hydrochloric acid and agitate to prevent caking. When dissolved add carefully 10 c.c. of concentrated sulphuric acid, fume, cool and add 300 c.c. of boiling water plus 25 c.c. of hydrochloric acid. Simmer to dissolve the sulphates while stirring with a glass rod. Filter through a Postlip Mills filter paper, using a glass-wool pad in a suction filter. Wash five times with hot water plus hydrochloric acid. Ignite and weigh. The weight multiplied by 200 gives the percentage of silica in the slag.

Lime.

Take 0.271 g. of finely ground sample, place in a 250-c.c. beaker, add 5 c.c. of hot water plus about 0.5 c.c. of hydrofluoric acid and 5 c.c. of hydrochloric acid. Agitate to prevent caking. When dissolved add 100 c.c. of hot water, bring to the boil and add a mixture of 10 c.c. of

20% ammonia plus 70 c.c. of precipitating solution (*see below*). Allow to settle. Filter with the aid of suction, using a Munktell paper and a pad of glass wool for the funnel. Wash five times with hot water. Dissolve the precipitate and paper in 100 c.c. of boiling water plus 10 c.c. of dilute sulphuric acid (1:1). Boil and titrate with *N/10* potassium permanganate; the number of cubic centimetres required gives the percentage of lime.

Precipitating Solution.

Ammonium tartrate	120 g.
Ammonium chloride	100 g.
Ammonium oxalate	100 g.
Water	6000 c.c.

Sulphur.

Estimated by evolution on the open-hearth floor. When necessary the Meinel-Silverman method is used.

Phosphorus.

Estimated by alkimetric titration of phospho-molybdate.

Silicon-manganese spring steels are cast into wide-end-down 25 × 21-in. corrugated moulds with an inserted tile sink-head. The sink-head volume is approximately 15% of the total ingot volume. Experience has shown that there is no exaggerated primary piping. The choice of mould depends upon :

(a) The evaluation of quality for the proposed application of the steel.

(b) Economy.

(c) Ease of operation. This mould has done a satisfactory job for years, is easily set up for casting and saves crane power.

In reply to Mr. Reed, it would be idle to say that deep-bath furnace bottoms are as easily manipulated as those of shallow-bath furnaces. However, no undue difficulty arises when compressed air at 80–100 lb. per sq. in. pressure is used through two 1-in. pipes for draining holes. This method is quick and efficacious, and can be applied to most sections of the banks and bottom.

Dust does collect in the grooves of a ribbed roof. If it is allowed to accumulate it becomes an excellent insulator and rapid roof wear follows. It is standard practice here to blow the roofs down once per week with compressed air. We have no difficulty in removing dust.

The furnace pressure-control equipment is of standard design. A 2-in. pipe connection is taken from the centre of the roof to a bell-type control unit mounted on the instrument panel. This controller actuates a motor-driven stack damper through electrical relays. It may be operated manually or automatically. The controlled pressure is adjustable and is normally operated in this shop at +0.05 in. water gauge under the roof. This setting gives a slight positive pressure at the inspection and sampling holes about 18 in. above the sill-plate level. The equipment is sufficiently sensitive to respond to pressure changes resulting from furnace

reactions and it normally operates continuously on the automatic setting except when sampling. During sampling the pressure controller is switched to manual operation and the pressure is reduced for the comfort of the crew.

Fresh water is expensive here and we do get corrosion troubles with salt-water cooling. The choice of cooling water is purely a matter of economy.

Mr. Mather's interest in shop tonnage is noted. *A* and *F* furnaces during the past six months have averaged 232 tons and 247 tons per heat, respectively. In the past twelve months tonnages have been stepped up considerably towards the true shop capacity and the peak has by no means been reached yet.

The stripping and transfer method operated here works very satisfactorily, and since the paper was published a third combination wall-type machine has gone into service. The main feature of this system is the saving in fuel resulting from the charging of ingots to the soaking pits at high temperature.

I agree with Mr. Mather that the question of open-hearth mechanical auxiliaries is one which does not always receive the attention it deserves and much tonnage is lost because of the failure to service furnaces with speed.

Dr. Swinden has, with other steel men, raised the question of slag volume and iron quality. Mr. Kilby has kindly elaborated extensively on this in his valuable written statement, and it is proposed to discuss this question in reply to Mr. Kilby.

It is regretted that Dr. Swinden has been misled on the question of ingot casting at Kembla by the view shown in Fig. 1. All ladles are equipped with two stoppers, and two ingots are cast in line. We do not cast two rows. The practical care of ingot moulds and stools is not satisfactory when using the two-row system.

In reply to Dr. Binnie, we compute the fuel consumption in the open-hearth by metering the tar and coke-oven gas to the furnaces individually. The gross calorific power of the coke-oven gas is continuously recorded at the coke-ovens and the tar value is estimated once per week. The B.Th.U. figure per ton is, therefore, calculated from the consumption of these fuels in the period divided by the weekly tonnage. There are no week-end shut-downs. The fuel used during "gas-on" delays is included in the figure.

Bottom-pouring experiments were tried some years ago and abandoned. We make no grade of steel warranting the appreciable extra cost of ascension pouring. Rimmed steel for automobile sheets is top-cast, and an excellent surface is obtained.

Mr. Jolly is partly correct in assuming that sand is used to obtain silica conveniently and cheaply. Structural steel is made to a 0.06% phosphorus maximum in Australia. Our product regularly contains under 0.03% of phosphorus and the quality is not in any way prejudiced by the presence of this amount.

In reply to Mr. Myers, we have no evidence to show that the insulation of furnace bottoms increases bottom repairs. We have not yet had occasion to tear out an insulated bottom and, therefore, have no indication of the condition of the insulating refractory. Bottom life in this country is 15 years plus.

With reference to Dr. Chesters' contribution, we did refer to rotary-kiln dolomitic refractories of American origin when discussing fettling materials. It is surprising that these particles are rounded. Recently we have been assured that the sizing is excellent and the particles are angular in shape. Sharp-edged irregular particles seem to be particularly desirable. Such material has a steeper angle of repose on the furnace banks and will not roll to the bottom, building it up and necessitating delays for washing out.

Raw dolomite is crushed to $-\frac{1}{2}$ in. It is not free from dust and has no specific advantages over burnt dolomite. Its use is governed by supply and cost.

Average fettling times would be 15–20 min. on 150-ton furnaces and 20–25 min. on the larger furnaces. The plant average consumption of bank and bottom materials is:

Raw dolomite	60 lb. per ton of ingots.
Burnt dolomite	6.5 " "
Calcined magnesite	2.5 " "

The consumption of material does increase with the age of the bottom.

We have not found bauxite to increase bank damage. The condition here is so obviously different from that in England. We do not have the thick high-lime slags to contend with and our usage of bauxite has never exceeded 2 lb. per ton of ingots. There can be no doubt that the incidence of bank erosion and bottom troubles increases with high-lime slags with high FeO contents. This is most pronounced in the production of low-carbon rimming stock, especially ingot irons.

In the past we have followed the practice of fettling the bottom and banks with $1\frac{1}{2}$ in. of fresh grain burnt magnesite before charging ingot-iron heats.

Referring to Mr. Wood's enquiries, the 1200-ton mixer is located in a 90-ft. bay alongside A furnace at the western end of the shop. The hot-metal crane is on the same track as the overhead charging machines and has to travel 675 ft. approximately to fill G furnace.

In reply to Mr. Sinclair Kerr, a special department exists for the maintenance of all works instruments. Until recently all instruments were imported, and it was necessary, in the absence of facilities for overhaul and repair by the makers, to set up a comprehensive repair service within the organisation. Equipment has been provided for the calibration and repair of all types of instruments, including the checking of optical pyrometers against National Physical Laboratory Standards. Routine daily inspections are made in accordance with a regular maintenance schedule and all

instruments are removed during furnace campaign repairs for overhaul.

A history card for each instrument is commenced at the date of purchase, and details of every repair and calibration are recorded thereon. This has proved invaluable, and a study of such records has resulted in the standardisation of equipment for similar applications throughout the works.

With reference to tar and coke-oven-gas firing, the method of atomising the tar has been modified since the paper was written. Large-scale experiments are proceeding and the results are encouraging. We have run *G* furnace for some weeks with 35% of the heat input derived from tar and 65% from coke-oven gas.

The value of the disappearing-filament type of optical pyrometer for temperature control has, after some years, been proved on this plant. The readings are necessarily comparative and the maker does not guarantee the instrument to an accuracy greater than $\pm 15^{\circ}$ F. We are convinced that in the hands of experienced observers readings are reproducible and can be applied with confidence. When pouring-temperature ranges are narrow we actually programme the bath temperature at tapping with very good results in the pouring pit.

Referring to Mr. Russell's contribution, the Kembla system of charging the furnaces does a good job when the burden is limited to works return scrap. The question of charging systems is largely one of geography and economy.

In the U.S.A. scrap is relatively cheap compared with hot metal, and therefore open-hearth designers have built their shops to handle maximum quantities of scrap. Should such conditions ever apply in Australia, the existing Kembla system could be readily modified to meet the change. The existing scrap-yard would perhaps be the marshalling yard only. The scrap could be loaded into pans at a remote scrap-yard. The existing charging-floor facilities would be adequate.

The ingot transfer cars have a capacity of six ingots at one time and the average distance of travel to the soaking-pit cranes is 450 ft.

We do not burn-out producer-gas furnaces at week-ends. Dust-catchers at the gas house are emptied after each heat, and this is generally completed before fettling finishes. The main raw-gas flue beneath the scrap-yard is blown out after the tenth week of operation. All furnaces are continuously worked without a week-end break.

We have had no trouble at all with the wide jack arches in the checker chambers and slag pockets. In nearly three years of operation not a single brick has been replaced in the generator arch of *F* furnace and, to date, the *G* furnace arches have been just as successful. The bridge walls on *G* furnace have been partially replaced once in two years of operation.

The most recent producer-gas-furnace figures to the mid-campaign repairs are:

	B Furnace.	E Furnace.
Nominal capacity	200 tons	150 tons
Normal fuel	Producer gas and coke-oven gas.	
Number of weeks operated	17½	14½
Number of heats	179	194
Average tons per heat	206.7	147
Total tonnage	37,013.00	28,593.00
Average tonnage per week	2,106.00	1,943.00
Approximate percentage of—		
Hot metal	65	65
Scrap	18	18
Fuel consumption:		
Equivalent coal. Lb. per ton	517	551
B.Th.U. per ton	6,979,500	7,440,500

The bifurcated launder used is shaped as a perfect Y. The distribution depends on the accuracy of the set-up and to some extent on the shape of the tap-hole. Where precisely controlled distribution is necessary, a short, heavily weighted stopper assembly is held by the crane in the V of the launder to ensure equal flow into both legs.

It is difficult to answer Mr. Russell's query about the saving in time with flush slag. Since the process depends entirely on correct timing, care is taken to see that furnaces are filled on time, as the graph in Fig. 6 would indicate. However, we should estimate that such a heat would take 2-3 hr. longer.

In reply to Dr. Leckie, it is a fact that in the high-hot-metal practice established at this plant the fuel input has to be strictly limited during possibly 2-3 hr. of the heat. During the ore reaction the fume is so great that the roof cannot be sighted from No. 2 to No. 5 door on the outgoing end. The danger of roof damage is real and this slows up the process.

We do not agree with Dr. Leckie that design can be a matter of indifference. Modifications to design are constantly being made, and we are convinced that these furnaces can be further improved from a tonnage and repairs and maintenance point of view. This is justified below in the reply to Mr. Kilby.

Referring to Mr. Kilby's contribution, initially we quoted further evidence of progress made at Kembla during the past two years. Comparing the performance of G furnace's initial campaign with that of the current run we have:

	Initial Campaign, concluded 9/12/41.	Current Campaign at 23/10/43.
Days operated	175	149
Heats	257	230
Average tons per week	2,289	2,616
Average tons per heat	223	242
Fuel consumption	3.861×10^6 B.Th.U.	3.847×10^6 B.Th.U.
Tonnage of ingots	57,238	55,685

The best weekly tonnage during the present campaign was 3,273 tons for the week ended 28/8/43, when the tonnage per hour was 20.28.

I thank Mr. Kilby for his interest and his valuable contribution. Without being in a position to check his figures on relative furnace potentials using 60–80% of hot metal on phosphoric irons, it must be agreed that as the slag ratio increases the output rapidly falls.

Mr. Kilby's reference to deterioration in quality is not quite understood. Such open-hearth charges are unknown in Australia, but it is possible to make a hypothetical case against the high slag volumes usually carried when working such heats. We note that some efforts have been made to use flush-slag practice with such burdens, but do not comprehend why the method has apparently met with little success.

Applying Lincolnshire conditions to a large furnace and charge we could have :

Furnace Charge.

Material.	Tons.	Total Metallics. %.	Phosphorus Content. %.
Mill return scrap	35	13.5	0.030
Mixer metal (Si 0.8%)	195	75.6	1.6
Lump ore	46	10.7	Low

The total phosphorus in the burden would be 3.121 tons.

Assuming that with perfect timing (for success the timing must be perfect) 25 tons of run-off slag could be reasonably taken, the P_2O_5 content of this slag could, if the flush were taken within one hour of filling, reach 20%. Hence the P_2O_5 left in the furnace would be 0.88 ton.

Therefore, if 20 tons of stone of 50% lime content were charged beneath a portion of the scrap and all the ore, the slag volume with 40% of lime in the slag would be approximately 25 tons, or about 11%. The P_2O_5 in the finishing slag would therefore be 3.5% approximately. The saving in furnace time is obvious.

It is understood that large quantities of phosphoric slag are sold to the fertiliser trade and perhaps economics influence the process used.

The flush-slag process will not be a success in any shop, regardless of the iron quality, if the organisation and equipment do not permit perfect timing. Furnaces must be filled on time and regular quantities of flush slag taken from heat to heat.

It is pleasing to note that Mr. Kilby expects a 25% increase in output from the all-basic furnace. This is the highest claim that has yet come to notice. The all-basic furnace may prove to be one of the largest cost-saving innovations in the history of the process.

In conclusion I would like to thank all those who commented on the paper for their interest and valuable contributions to the discussion.



OBITUARY.

Dr. WILLIAM HERBERT HATFIELD, F.R.S., Technical Research Director of Messrs. Thomas Firth and John Brown, Ltd., also a director of Messrs. Firth-Vickers Stainless Steels, Ltd., died at his home, Brincliffe House, Osborne Road, Sheffield, after a short illness, on Sunday, October 17th, 1943, at the age of sixty-one.

The son of the late Francis Albert Hatfield, Dr. Hatfield was educated at University College, now the University, Sheffield, where he received his early metallurgical training under the late Professor J. O. Arnold. He obtained his first prize in the field of practical metallurgy in 1899, and in 1902 he won the Mappin Medal. His first industrial experience, appropriately enough, was in the works of Sir Henry Bessemer and Co., Ltd., from which he moved to Messrs. J. Crowley and Co., of Wincobank, Sheffield. In 1916 he was appointed Director of the Brown-Firth Research Laboratories, which position he still held at the time of his death.

It was in 1902 that, in collaboration with Professor McWilliam, who was then senior lecturer in metallurgy at University College, Sheffield, he presented his first paper to The Iron and Steel Institute; this was on the elimination of silicon in the acid open-hearth furnace. In the same year he received a grant from the Andrew Carnegie Research Fund to enable him to study the influence of the condition of the carbon on the properties of cast iron; he showed that malleable cast iron might be produced with an elongation of 15–20%, the ruling characteristic up to that time being an elongation of about 3–6%. He published several technical papers on this subject. Dr. Hatfield was author of a text-book, "Cast Iron in the Light of Recent Research," and also contributed very many papers to scientific societies and the technical press, including the following to The Iron and Steel Institute:

"The Elimination of Silicon in the Acid Open-Hearth." (With A. McWilliam; *Journal*, 1902, No. I.)

"Acid Open-Hearth Manipulation." (With A. McWilliam; *Journal*, 1904, No. II.)

"Influence of the Condition of the Several Varieties of Carbon upon the Strength of Cast Iron as Cast and Heat-Treated." (*Journal*, 1906, No. II.)

"Cast Iron as Cast and Heat-Treated." (*Journal*, 1907, No. II.)

"The Chemical Physics Involved in the Decarburisation of Iron-Carbon Alloys." (*Journal*, 1909, No. I.)

"The Influence of Vanadium upon the Physical Properties of Cast Iron." (*Journal*, 1911, No. I.)

"Influence of Sulphur on the Stability of Iron Carbide in the Presence of Silicon." (*Journal*, 1913, No. I.)

"Phosphorus in Iron and Steel." (*Journal*, 1915, No. II.)

"Report on the Present Position of the Malleable Castings Industry in this Country." (*Journal*, 1917, No. II.)

"The Influence of Nickel and Chromium upon the Solubility of Steel (in Relation to Corrosion)." (*Journal*, 1923, No. II.)

"Heat-Resisting Steels. Part 1." (*Journal*, 1927, No. I.)

"Heat-Resisting Steels. Part 2." (*Journal*, 1928, No. I.)

"Permanence of Dimensions under Stress at Elevated Temperatures." (*Journal*, 1930, No. II.)

"The Influence of Beryllium on Steel." (With J. H. S. Dickenson; *Journal*, 1933, No. II.)

"Investigation to Determine the Value of the Proposed Laboratory Tests [of the Corrosion Committee]." (With H. T. Shirley; *Special Reports No. 1*, 1931, and *No. 2*, 1934.)

"The Work of the Corrosion Committee." (*Special Report No. 11*, 1936.)

"The Work of the Heterogeneity of Steel Ingots Committee." (*Special Report No. 12*, 1936.)

"Subsidiary Corrosion Tests on the Low-Alloy Structural Steels Exposed in Part III. of the Corrosion Committee's Experimental Programme." (With H. T. Shirley, T. Swinden, W. W. Stevenson, J. C. Hudson and T. A. Banfield; *Special Report No. 13*, 1936.)

"A Study of a Nickel-Chromium-Molybdenum-Vanadium Steel Ingot." (*Special Report No. 25*, 1939.)

"Non-Metallic Inclusions in Steel. Quantitative Evaluation. Part 1." (With G. W. Giles; *Journal*, 1940, No. II.)

On his appointment as Director of the Brown-Firth Research Laboratories, Dr. Hatfield's interests became centred essentially in alloy steels and to some extent also in some of the non-ferrous metals. It is with the field of rust-, acid- and heat-resisting steels that his name is principally associated. He studied the influence of increasing quantities of chromium in the original stainless steel, as well as the effect of nickel additions, and was thus the first to demonstrate the special qualities of what is now universally known as 18/8 austenitic chromium-nickel stainless steel; later, he succeeded in developing 12/12 austenitic chromium-nickel corrosion-resisting steel, which is more ductile. The pioneer investigations of the phenomenon of intercrystalline corrosion of the 18/8 steel were successfully carried out by him in the Brown-Firth Laboratories, and he was the first to indicate the possibility of counteracting that tendency by the addition of other elements. This sphere of his work received special mention at the Annual General Meeting of The Iron and Steel Institute in 1933 when the Bessemer Gold Medal was presented to him by the President, Mr. W. R. Lysaght.

If Dr. Hatfield's name is primarily associated with stainless steels, yet of scarcely less importance was his work and stimulating interest in the organisation of research. He rendered most valuable service to The Iron and Steel Institute as Chairman of the Heterogeneity of Steel Ingots Committee, of the Corrosion Committee and of the Alloy Steels Research Committee, inaugurated in 1924, 1928 and 1934, respectively. All three of these Committees, over which he had presided since their foundation, are now being carried on jointly by the Institute and the British Iron and Steel Federation, under the auspices of the Iron and Steel Industrial Research Council. These Committees were to him like personal hobbies, and it was only

natural that he should, in later years, be appointed Chairman of the Programme and Finance Committee of the Research Council.

Dr. Hatfield, who had joined the Iron and Steel Institute in 1903, was elected to the Council in 1927 and became a Vice-President in 1934. In addition to his long and active interest in all matters concerning the Institute, he was associated with and honoured by many other technical societies. He founded the Sheffield Metallurgical Society, of which he was the first President. He was President of the Sheffield Society of Engineers and Metallurgists for three years. He became a Member of Council of the Sheffield University and was also a Fellow of the Chemical Society, a Fellow of the Institute of Physics, a Fellow of the Institution of Chemical Engineering, a Member of the Institution of Mechanical Engineers, and, in 1935, became a Fellow of The Royal Society. He was awarded the Compton Medal of the Institution of Automobile Engineers. In 1928, by unanimous invitation of the American Society for Metals, he delivered the Campbell Memorial Lecture at Philadelphia, and in 1938 he delivered the Tenth Gluckstein Memorial Lecture to the Institute of Chemistry.

A full account of Dr. Hatfield's war-time activities cannot be given at the present time, but it can be said that he was largely responsible for convincing the authorities that, in spite of the concentration of effort on increased iron and steel production, it was necessary for research work to continue. He served on several committees set up to deal with problems connected with the war, a very important one being the Technical Advisory Committee on Special and Alloy Steels, of which he was Chairman. Together with a group of well-informed metallurgists and representatives of Service Departments, this Committee undertook a revision and rationalisation of the innumerable specifications for special and alloy steels, which resulted in the issue of the "En" series of specifications. In addition, he was Chairman of a series of technical committees on armour, of the technical committee advising the Iron and Steel Control, and of a small committee responsible for the examination of enemy aircraft and other components. Within the last year he was one of several delegates sent to the United States to foster a still closer co-operation between the metallurgical industries of Great Britain and America.

It can truly be said that he died for his country, through strain and overwork in furthering the war effort, for in the last four years he had had no holiday. Perusal of his book "Sheffield Burns," which he did not live to see published, reveals the intense love he had for his native city of Sheffield and his belief in individualism and that the key to reconstruction and achievement is hard work. Those who were privileged to work with or under him will always remember his enthusiasm, energy and untiring effort towards solving the problem in hand. He loved discussion and often put forward unconventional and challenging views to stimulate his hearers to

further efforts in the search for knowledge. With his passing the iron and steel industry in general and The Iron and Steel Institute in particular, mourn the loss of a great metallurgist, a leader of research and a friend.

Sir ROBERT STUART HILTON, O.B.E., died at his home at Shipston-on-Stour, Warwickshire, on October 10th, 1943, aged seventy-three. He was educated at Sedbergh School. He served his time as a mining engineer with the Wigan Coal and Iron Co., and later became manager of the Garswood Colliery of Messrs. J. R. Stone and Co. At the age of forty-one he was appointed manager of the Birmingham Corporation Gas Department. He served with the Royal Warwickshire Regiment in the last war, but, at the request of Lord Moulton, was seconded from his unit and appointed to organise the gas undertakings of the country for the manufacture of toluol and high explosives. He also served on the Birmingham Munitions Committee. For his services during the last war he was awarded the O.B.E., Military Division. In 1919 he was appointed Managing Director of the Metropolitan-Vickers Electrical Co., Ltd., Manchester, becoming Deputy Chairman in 1927. In the latter year he was invited by the Admiralty to preside over a committee to investigate and report on the costing system in operation in Naval Dockyards. He resigned this position in order to become Managing Director of The United Steel Companies, Ltd., in 1928 and held this post until 1939, being thus largely instrumental in building up the Company; from 1939 to 1942 he was Deputy Chairman. He was also on the boards of the following Companies: British Power and Light Corporation, Ltd.; Messrs. John Summers and Sons, Ltd.; North Wales Power Co., Ltd.; Templeborough Rolling Mills, Ltd.; Trent Valley and High Peak Electricity Co., Ltd.; and Messrs. William Cooke and Co., Ltd.; he was also Trustee of the Workington Harbour and Dock Board.

During his time with The United Steel Companies he took a keen interest in research, and it was due to his initiative that the Central Research Department of the group was formed and the laboratories were built and equipped. He was extremely active in improving the contacts in industry between workers and management, and also inaugurated many social measures, including the works and staff pensions scheme. At the time of the reorganisation of the structure of the steel industry under the Tariff Committee of Sir George May he was appointed Chairman of the Midland Group of Steel Manufacturers, and was President of the British Iron and Steel Federation from 1939 to 1942. He was knighted in the New Year's Honours in 1942. He was elected a Member of The Iron and Steel Institute in 1930, a Member of Council in 1931 and a Vice-President in 1940.

CHARLES JOHN BAGLEY, who died on March 1st, 1943, at Hartburn, Stockton-on-Tees, in his ninety-fifth year, was one of the

early pioneers of the steel trade on the North-East Coast. Born in the County of Durham, he received his early training at the Consett Ironworks, and subsequently spent over half a century on Tees-side, where his first appointment was that of general manager of the Tees Bridge Ironworks. He laid down the first steel plant at the Moor Works, Stockton, which afterwards became the property of the South Durham Steel and Iron Co., Ltd. It was only shortly before his death that he relinquished his seat on the board of that Company. He was a Past-President of the Cleveland Institution of Engineers. He joined The Iron and Steel Institute in 1873, was elected a Member of Council in 1906 and a Vice-President in 1915, and was made an Honorary Vice-President in 1924.

JAMES AUGUSTINE FARRELL died in New York on March 28th, 1943, at the age of eighty. As a youth of sixteen he was employed in a wire mill in New Haven, Connecticut, and, although working the then customary 12 hr. per day, he studied at home. A few years later he moved to the Pittsburgh Wire Co., where he became a foreman before he was twenty-one, sales manager at twenty-six and general manager of the whole organisation at the early age of thirty. That was in the panic year of 1893, when buyers were not taking steel. While others waited for the storm to pass, Mr. Farrell invaded the foreign field and sold half of his Company's output abroad.

In 1899, the Pittsburgh Wire Co. was merged to form the American Steel and Wire Co., and Mr. Farrell became foreign sales manager. Two years later, the United States Steel Corporation was formed, with the American Steel and Wire Co. as a subsidiary. In 1903, the United States Steel Products Co. was organised to co-ordinate the foreign activities of all the Corporation's subsidiaries, and Mr. Farrell became its first President. In 1911 he was made President of the United States Steel Corporation, a position which he held for twenty-one years.

As a leader in the steel industry, Mr. Farrell was active in the American Iron and Steel Institute, serving as a Vice-President and as Chairman of its Committee of Foreign Relations. For several years he was also Chairman of the Committee on Foreign Relations of the United States Chamber of Commerce. He was awarded the first Gary Memorial Medal by the American Iron and Steel Institute in 1929. Many other honours were bestowed upon him, including two decorations by the Vatican, honorary degrees by several universities, a commission in the French Legion of Honour and the Order of the Crown of Italy. As a Founder and Chairman of the National Foreign Trade Council, he worked continuously for foreign trade policies that would ensure world peace and break the barriers set up by preferential trading systems. He was often referred to as "The Dean of Foreign Trade." He became a Member of The Iron and Steel Institute in 1929 and was elected an Honorary Vice-President in the following year.

JAMES STANLEY ATKINSON died suddenly on September 18th, 1943, aged sixty-one. He was intimately connected with the iron and steel industry for many years. While travelling in France on behalf of Messrs. Wellman, Seaver and Head (now the Wellman Smith Owen Engineering Corporation, Ltd.), he met Mr. Stein, and this association resulted in the foundation, in 1915, of the firm Messrs. Stein and Atkinson, Ltd., the well-known furnace constructors and combustion engineers. He was a member of the Institution of Mechanical Engineers and of the Society of Glass Technology and a Fellow of the Institute of Fuel. He contributed many papers to the technical societies in which he was interested. He was elected a Member of the Iron and Steel Institute in 1913.

WILLIAM BARRASS, chief chemist of Messrs. Samuel Fox and Co., Ltd., died suddenly of heart failure on May 23rd, 1943. Mr. Barrass was elected a Member of The Iron and Steel Institute at the Annual Meeting only a few days before his death.

Colonel LIONEL BEAUMONT-THOMAS, M.C., J.P., of Great Brampton, Madley, who had previously been posted as missing, was officially reported killed in action on May 5th, 1943; he was fifty years of age. Born at Lydney and educated at Rugby, he received his early training in the steel industry at the Arbed Works, Luxemburg. He was for more than twenty-five years a director of Messrs. Richard Thomas and Co., Ltd., the steel, tinplate and sheet manufacturing firm in South Wales which was founded by his grandfather. In the last war he served in the Royal Horse Artillery and Royal Artillery Regiments in France and Italy, gaining the Military Cross and being mentioned in despatches. He rejoined the army at the outbreak of the present war. He was a member of the Haberdashers' Company and a Freeman of the City of London. He sat in Parliament as a Conservative for the King's Norton Division of Birmingham from 1929 until 1935. Apart from the Army and business he had other wide interests, following public affairs keenly and being an expert yachtsman. He was elected a Member of The Iron and Steel Institute in 1936.

LESLIE BRADFORD died at Toorak, Melbourne, after several months' illness, on June 20th, 1943, at the age of sixty-five. Born at Delhi, India, he accompanied his parents to Australia in 1892, and then started his forty-one years of service with the Broken Hill Proprietary Co., Ltd., at Port Pirie, where he entered the laboratory as an assayer. He had previously gained his diploma in mining and metallurgy at the South Australian School of Mines. In 1902 he became associated with the late Mr. G. D. Delprat in a series of experiments to solve the problem of lead and zinc sulphide recovery; this led to the patenting of the Delprat process. He

introduced many refinements to the flotation process, including, in 1912, a method of separating lead and zinc sulphides. His major contribution to flotation, however, was the discovery that a small amount of copper sulphate greatly increased the floatability of the zinc blende. This was an epoch-making discovery, the importance of which is illustrated by the fact that, throughout the world, every flotation mill now uses copper sulphate for the recovery of zinc concentrates. Thus, to him is due the honour of being one of the first to discover the use of retarding and accelerating agents in flotation. From 1912 to 1914 he was chief metallurgist at the Broken Hill Works and general superintendent of the flotation, zinc-roasting and acid plants. In 1915 the Broken Hill Company embarked upon the production of iron and steel at Newcastle, N.S.W. Mr. Bradford established the steelworks laboratory and tackled with thoroughness and energy the problems inseparable from the early efforts at successful steel production. He was appointed superintendent of the open-hearth plant in 1918, production superintendent at the Newcastle Steel Works in 1922, steelworks manager in 1924, and general manager of the Company in 1935. He was honoured on several occasions for his scientific and industrial achievements, receiving the Australasian Institute of Mining and Metallurgy Medal for 1937. He was also elected an Honorary Correspondent of the South Australian School of Mines, a member of the American Institute of Mining and Metallurgical Engineers, and to membership of The Iron and Steel Institute in 1930.

HUGH MYDDLETON BUTLER died at Burley, Leeds, on October 10th, 1943, at the age of eighty-six. He was a Director of Kirkstall Forge, Ltd., Leeds, probably the oldest iron-manufacturing establishment in the district, and represented the fourth generation of the family to be closely identified with the industry. He was a member of the Institution of Mechanical Engineers and of the Executive Committee of the National Federation of Iron and Steel Manufacturers (now the British Iron and Steel Federation). Since 1902 he had been Chairman of the North Leeds Conservative Association, and was Member of Parliament for North Leeds in 1922-1923. He was elected a Member of The Iron and Steel Institute in 1895.

WILLIAM POLLARD DIGBY, of Wood Green, London, who died on July 5th, 1943, at the age of sixty-seven, was a consulting mechanical and electrical engineer of wide experience. He was educated partly at home and partly at the Guildhall Middle School, Bury St. Edmunds, and then received training at the Crystal Palace School of Practical Engineering. After serving a pupilage at the Newton Electrical Works, Taunton, he went to New York in 1896 to study the electro-chemistry of the chlorine process. On his return to Great Britain he worked under Professor A. A. Kanthack

and Dr. S. Rideal on the sterilisation of sewage effluents. In 1901 and 1902 he was employed by the Buck Henrici Engineering Co., of Berlin, where he was in charge of the steam-engine test-bed and the drawing office. Returning to London, he was engaged on the design and testing of rotary engines, and was lecturer in engineering at his former school, the Crystal Palace School of Practical Engineering. Either by himself or in partnership he carried out many schemes and was responsible for the design of many power-stations, pumping-stations and industrial plants. He designed the Vibragraph, and, jointly with Mr. C. W. V. Biggs, was responsible for the design of the Dionic water-tester. He served in the Royal Engineers in the first part of the last war, and from 1916 to 1920 was attached to the Ministry of Munitions. He was a member of the Institution of Mechanical Engineers and of the Institution of Electrical Engineers, a Fellow of the Institute of Physics and a Member of Council of the Association of Consulting Engineers. He was elected a Member of The Iron and Steel Institute in 1938.

ALFRED RIX HABERSHON died on December 6th, 1943, at the age of sixty-two. A native of Rotherham, he was educated at Rotherham Grammar School, Wesley College, Sheffield, and Sheffield Technical School. As well as being Managing Director of Messrs. J. J. Habershon and Sons, Ltd., steel-strip manufacturers of Rotherham, he took an active part in civic affairs, for he was a member of the Rotherham Borough Council from 1911 to 1938. He was elected an Alderman in 1925 and Mayor in 1932. He was appointed a Justice of the Peace in 1928 and was made a Freeman of the Borough in 1939. He became a Member of The Iron and Steel Institute in 1926.

JOHN JENKIN ASHTON JONES died at his home in Sheffield on November 1st, 1943, at the early age of forty-nine. Receiving his scientific education at Aberystwyth College of the University of Wales, he obtained the degree of B.Sc. (Wales) in 1915, and subsequently the M.Sc. degree. He saw active service in the war of 1914-18 and was awarded the Military Medal. Leaving the Army in 1917 as a result of wounds, he joined the Research Department, Royal Arsenal, Woolwich, as research metallurgist and assistant to Dr. R. H. Greaves. Collaborating with Dr. Greaves in a series of researches on alloy steels, they presented to the Institute in 1920 a joint paper on "The Temper-Brittleness of Nickel-Chromium Steels." This was followed in 1925 and 1926 by three more joint papers, entitled "Temper-Brittleness of Steel; Susceptibility to Temper-Brittleness in Relation to Chemical Composition," "The Effect of Temperature on the Behaviour of Iron and Steel in the Notched-Bar Impact Test" and "The Ratio of the Tensile Strength of Steel to the Brinell Hardness Number." He was also author of the following papers to The Iron and Steel Institute :

"The Ac₁ Range in Alloy Steels." (*Journal*, 1923, No. I.)

"The Properties of Nickel Steels with Special Reference to the Influence of Manganese." (*Journal*, 1928, No. I.)

"High Elastic Limit Structural Steels." (*Journal*, 1929, No. II.)

"Chromium-Copper Structural Steels." (*Journal*, 1930, No. I.)

"The Effect of Phosphorus on the Mechanical and Corrosion-Resisting Properties of Low-Carbon and of Low-Alloy Structural Steels." (*Journal*, 1937, No. I.)

"The Effect of Chromium and Carbon Contents on the Coefficients of Thermal Expansion of Chromium Steels." (With W. C. Heselwood; *Journal*, 1938, No. I.)

In 1930 he joined the staff of The United Steel Companies, Ltd., and with Dr. T. Swinden, the Director of Research, took a large part in planning and equipping the Central Research Department of the Companies, at Stocksbridge. When the Department was opened in 1934, he was appointed manager, and during the last nine years of his life carried out or supervised much valuable work in several fields of research. He took an active part in the affairs of the Sheffield Metallurgical Association. He became an Associate of the Institute of Physics in 1920 and was made a Fellow three years later. He was elected a Member of The Iron and Steel Institute in 1920.

EDWARD F. KENNEY died on July 8th, 1943, at Media, Pennsylvania, aged seventy-four. He was widely known throughout the American steel industry, with which he had been associated since 1907. He was a Past-President of the American Steel Manufacturers' Association, which was later absorbed by the American Iron and Steel Institute, and was senior member of several committees of the American Society for Testing Materials. He had also served on the Technical Advisory Committee of the War Production Board. He was metallurgical engineer on the staff of the Bethlehem Steel Company. He was elected a Member of The Iron and Steel Institute in 1912.

CARL KING, of Palmer, Massachusetts, died on June 25th, 1943, aged sixty-three. He held an executive position with the American Steel and Wire Co., Worcester, Mass., and in 1920 became associated with the Wickwire Spencer Steel Co., in which Company he rose to the position of general superintendent. He was elected a Member of The Iron and Steel Institute in 1928.

FITZHERBERT ALBERT BUGBY LORD died on January 19th, 1943, at the age of eighty-one. He spent the whole of his working life in the service of Messrs. W. F. Dennis and Co., Ltd., iron, steel and wire merchants, of which Company he became Principal in 1902, and Chairman in 1937, when it was made a limited company. He was a Member of the Court of Common Council and Deputy of Cordwainer Ward of the City of London. He was elected a Member of The Iron and Steel Institute in 1910.

JOHN PATON, J.P., of Llanvair Grange, Abergavenny, died after a short illness on February 18th, 1943, at the age of seventy-nine. He was the principal shareholder as well as Chairman and Managing director of Messrs. Partridge, Jones and John Paton, Ltd., the important South Wales colliery company with steel and tinplate interests. He had other extensive interests in the tinplate and coal industries, and was Chairman of a number of colliery companies. He was also a Director of the Cambrian Insurance Co., Ltd., and had been a Director of Messrs. Guest Keen and Nettlefolds, Ltd., for eleven years. He was elected a Member of The Iron and Steel Institute in 1887.

ERIC RAYMOND RAWLIN died at his home at Greasborough, near Rotherham, on January 11th, 1943, at the age of forty-five. He was on the metallurgical staff of the Park Gate Iron and Steel Co., Ltd., with which firm he had been for twenty-four years. He was elected a Member of The Iron and Steel Institute in 1936.

Professor ARTHUR AVERY READ died suddenly at his home in Bournemouth on September 24th, 1943, at the age of seventy-five. Educated at Exeter Grammar School and at Owens College, Manchester, he later entered the University of Sheffield and studied metallurgy under the late Professor J. O. Arnold, obtaining the degree of M.Met. in 1907. He remained on the staff of the University for some years, during which he conducted a series of researches, several of them in collaboration with Professor Arnold, on the influence of the carbides of chromium, nickel, tungsten, vanadium, cobalt and molybdenum on the chemical and mechanical properties of various alloy steels. He and Professor Arnold presented two papers entitled "The Chemical and Mechanical Relations of Iron, Chromium and Carbon" and "The Chemical and Mechanical Relations of Iron, Vanadium and Carbon," in 1910 and 1911, respectively, before The Iron and Steel Institute, in which the results of some of this work were made known. For his work in this field, much of which was of a fundamental character, he was awarded the degree of D.Met. (Sheffield). Meanwhile he had been appointed Professor of Metallurgy at the University College of South Wales and Monmouthshire, Cardiff, and began work on various non-ferrous alloys. The first of these dealt with the influence of phosphorus on some copper-aluminium alloys. This was followed by a series of investigations on nickel-aluminium and copper-nickel-aluminium alloys, conducted in association with Dr. R. H. Greaves. For this and other work Professor Read received the honorary degree of D.Sc. (Wales). He retired ten years before his death and was made Professor Emeritus. He was elected an Associate of the Royal Institute of Chemistry in 1889, becoming a Fellow in 1895; he was also a Fellow of the Chemical Society. He became a Member of The Institute of Metals in 1913 and of The Iron and Steel Institute in 1920.

HARRY MACKENZIE RIDGE, died on August 4th, 1943, aged seventy. He was born in London and received his early education at Christ's Hospital in the City. Later he studied mining engineering and mine surveying at Freiberg in Saxony, obtaining the diploma of Bergingenieur und Markscheider. He went to Australia in 1899 as manager of the Australian Metal Company's works at Broken Hill, and occupied this position until 1905, when he returned to England to become general manager of the Central Zinc Co., Ltd., Seaton Carew, Co. Durham, and a Director of the Central Acid Co., Ltd. In 1909 he relinquished his position with the Central Zinc Company and began to practice as a consulting mining and metallurgical engineer. He was perhaps best known for the Ridge roasting furnace, and, as Principal of the Ridge Roasting Furnace and Engineering Company, was responsible for the erection of numerous metallurgical plants throughout the world. He was associated with the Imperial Institute Intelligence Section and was one of the most active members of the Imperial Institute Consultative Committee on Base Metals. He took a great interest in the activities of The Iron and Steel Institute, which he joined in 1908, and was a regular attendant at its meetings both in this country and abroad.

FRANK SCOTT RUSSELL died at Cheltenham, after a long illness, on September 8th, 1943, at the age of sixty-five. Born at Hull and educated in Sunderland, he entered the refractories industry in 1900, receiving training with Messrs. J. Grayson Lowood and Co., Ltd., Sheffield, and the Steetly Lime Co., Ltd., Worksop. He helped to found the Kelham Island Firebrick Co., Ltd., Sheffield, and subsequently became Chairman and Managing Director of General Refractories Ltd., Sheffield, a position he held until 1939. He was a Fellow of the Geological Society and of the Entomological Society, a member of the Institute of British Foundrymen and of the Institute of Metals, a Vice-President of the Institute of Quarrying and a Founder and Past-President of the Refractories Association of Great Britain and of the National Association of Clayworks Managers. He was a man of great energy and bold ideas, and many of the trade and technical activities of the refractory industry owe much to his initiative and support. He was elected a Member of The Iron and Steel Institute in 1915.

FREDERICK GEORGE SMITH died at the age of fifty-nine at his home in Purley, Surrey, on March 1st, 1943. He was educated in a private school at Hitchin and at Harpur School, Bedford, after which he completed five years' apprenticeship with the Bedford Engineering Co. His next position was that of junior draughtsman with Messrs. Jessop and Appleby of Leicester. In 1906 he began his long connection with the Wellman Smith Owen Engineering Corporation, Ltd., the firm being then known as Messrs. Wellman, Seaver and Head. He held in succession the positions of assistant chief

draughtsman, chief draughtsman, assistant engineer, chief engineer, chief engineer and manager, Director and finally, in 1919, Director and technical manager. While with this Corporation he was responsible for the design of all the firm's products, including metal mixers and furnaces, charging machines, ladles and magnetic cranes. Several complete steelworks were built under his supervision, including plant for Messrs. Alfred Hickman, Ltd., Bilston. He was also a Director of the Wellman Seaver Rolling Mill Co., Ltd. He was a member of The Institution of Mechanical Engineers and was elected a Member of The Iron and Steel Institute in 1913.

JULIUS LENNARD FOX VOGEL died at Sandy, Bedfordshire, on August 30th, 1943, in his seventy-first year, after a short illness. He was the youngest son of the late Sir Julius Vogel, K.C.M.G., a former Prime Minister of New Zealand, and was educated at Charterhouse. He served two years' apprenticeship with the Gulcher Electrical Engineering Co. and also attended the Finsbury Technical College. In 1895 he was appointed assistant manager to the Chemical and Electrolytic Syndicate, Ltd., under the late Dr. O. J. Steinhart, with whom he later entered into partnership; this firm practised as consulting metallurgists and chemists until 1907, when the partnership was dissolved. Until 1914 he was engaged upon large-scale experimental work in electro-chemistry and on accumulators. Subsequently he specialised in alloy steel and iron developments and in 1914 designed, erected and started a factory at Widnes for High Speed Steel Alloys, Ltd., for producing tungsten, molybdenum and vanadium. He was appointed general manager of the works, a position which he held until his death. He was a member of the Institution of Electrical Engineers, of the Institution of Chemical Engineers and of the Institution of Mining and Metallurgy. He was elected a Member of The Iron and Steel Institute in 1918, and served on the Alloy Steels Research Committee.

ROBERT GUTHRIE WOODWARD died on August 27th, 1943, at the age of sixty-two, after a long illness. Educated at Giggleswick School, he joined Messrs. Edgar Allen and Co., Ltd., of Sheffield, in 1898 and received practical and commercial experience in all departments of their works. He studied metallurgy and electrical engineering, and in 1907 spent nine months in South Africa and Rhodesia as a representative of the above Company. He was a lay reader in the Church of England, a member of the Sheffield Chamber of Commerce and a former Chairman of the Sheffield branch of the Incorporated Sales Managers' Association. He was elected a Member of The Iron and Steel Institute in 1904.

SECTION II.

A SURVEY OF LITERATURE ON THE MANUFACTURE AND PROPERTIES OF IRON AND STEEL, AND KINDRED SUBJECTS.

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and Dr. D. R. STEINER.

ORES—MINING AND TREATMENT

Mechanical Skip Loading Underground. J. Hedlund, B. Wickbom and I. Janelid. (*Jernkontorets Annaler*, 1943, vol. 127, No. 1, pp. 1-33). (In Swedish). This paper constitutes the Report of a committee appointed in March 1941 by the Mining Investigation Committee of Jernkontoret to study mechanical loading in mines. It contains a comprehensive survey of data obtained on the working of Atlas and of Eimco loading machines of different capacities in some of the Swedish iron-ore mines.

Flotation of Tungsten Ores. D. C. McLaren. (*Canadian Mining Journal*, 1943, vol. 64, Jan., pp. 8-13). The author discusses the nature and use of addition agents, promoters, froth modifiers and frothing agents in the flotation of scheelite and other tungsten-bearing ores.

Beneficiation of Some British Columbia Tungsten Ores. J. M. Cummings. (*Canadian Mining and Metallurgical Bulletin*, 1943, Feb., pp. 47-69). The author reports on laboratory and full-scale tests of methods of concentrating some of the tungsten ores found in British Columbia, where there are at present two mills treating scheelite.

Future Possibilities of Mesaba Magnetite Sinter. G. W. Hewitt. (*Eastern States Blast Furnace and Coke Oven Association: Blast Furnace and Steel Plant*, 1942, vol. 30, July, pp. 753-757; 768). The author considers the economic aspects of the large-scale sintering of the magnetic taconite ores of the Mesaba Range, and calculates the advantages in cost of shipping a sinter containing 64% of iron as against supplying a standard ore containing 51.50% of iron.

Sheet and Tube now Operating New Modern Sintering Plant. (*Iron and Steel Engineer*, 1943, vol. 20, Jan., pp. 46-48). An illustrated description is given of the recently completed sintering plant at the Campbell Works of the Youngstown Sheet and Tube Co. (*See Journ. I. and S.I.*, 1943, No. I., p. 189 A).

REFRACTORY MATERIALS

Equilibrium Relationships on the Liquidus Surface in Part of the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ System. R. B. Snow. (*Journal of the American Ceramic Society*, 1943, vol. 26, Jan., pp. 11-20). The author describes an investigation to determine what crystalline solid phases are in equilibrium with cristobalite, tridymite, mullite and corundum on the liquidus surface in the system $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ and to establish the temperature and composition of each of the

quintuple points involved. The conclusions reached were: (1) The fields of tridymite, cristobalite, mullite and corundum probably occupy more than two-thirds of the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ system. (2) Two compounds with MnO , Al_2O_3 and SiO_2 as essential constituents have a stability range on the liquidus surface; they have been identified as spessartite, $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$, and a manganese mineral with the approximate composition $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, which seems to have a basic structure similar to cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. (3) A third crystal type, referred to as "extinction" crystals, crystallised from a small range of composition, but it may be eliminated by heating during the preparation of $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. (4) Spessartite probably melts congruently at 1200°C .; the $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ melts incongruently to form mullite and a liquid, the upper limit of this reaction is 1200°C . (5) Crystals of $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ have the same structure as the spessartite variety of garnet. (6) In that part of the systems $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2\text{-SiO}_2$, $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-SiO}_2$ there are present one eutectic quintuple point and four peritectic quintuple points. These quintuple points include point 1, a eutectic involving the phases tridymite, spessartite and $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$; point 2, a peritectic involving $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, tridymite and mullite; point 3, a peritectic involving $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, spessartite and corundum; point 4, a peritectic involving $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, mullite and corundum; and point 5, a peritectic involving spessartite, corundum and galaxite. (7) Two quintuple points have been tentatively established; point 6, a eutectic involving rhodonite, spessartite and tridymite; and point 7, a eutectic involving rhodonite, spessartite and tephroite.

Silica and Semi-Silica Refractories. J. H. Chesters. (Iron Age, 1943, vol. 151, Jan. 21, pp. 36-41; Jan. 28, pp. 44-47). The author discusses the behaviour of silica brick at different temperatures, its reactions with oxides, the raw materials for making silica bricks, the properties of semi-silica bricks and the prevention of silicosis. Until recently most German silica bricks were made from the Findlings quartzites, which are of small, but varying, grain size; this quartzite is converted to cristobalite and tridymite much more rapidly than a Sheffield ganister or a Welsh quartzite. Lime speeds up the conversion of quartz to cristobalite, whilst iron oxide accelerates the production of tridymite. Other mineralisers, such as phosphates and alkalis, have been used from time to time in making silica bricks, but they have mostly been replaced by mill-scale. Sand-clay bricks containing about 88% of silica are known as semi-silica or sand bricks. Their properties are intermediate between those of silica bricks and fireclay bricks. They are essentially volume-constant in use, have a higher thermal-shock resistance than silica brick and tend to glaze very readily.

High Temperature Heat Insulation. G. W. Paterson. (Canadian Ceramic Society: Canadian Metals and Metallurgical Industries,

1943, vol. 6, Jan., pp. 6-11, 33). The author discusses heat insulation, the various forms in which it is available and its effects on the fuel economy of furnaces in general, citing some examples of applications in metallurgical industries.

Practical Aspects of Industrial Furnace Insulation. J. W. Dawson. (*Metallurgia*, 1943, vol. 27, Mar., pp. 177-180). The author considers the advantages and limitations of insulating refractories for industrial furnaces. High- and low-temperature insulating bricks should be used in conjunction with each other as complementary components whenever conditions permit, but mechanical stability must have first consideration. There are instances of furnaces previously lined with firebrick and subsequently adapted to hot-face insulation in which the time required to reach the working temperature has been reduced by 80%.

Latest Developments in Refractories. C. L. Norton, jun. (*Heat Treating and Forging*, 1942, vol. 28, Sept., pp. 474-476). The author discusses the advantages of insulating firebricks and presents tables of data showing the transmitted heat losses and heat-storage capacities of different types of wall construction with and without a covering of insulating bricks.

FUEL

Water Problems in Small Power Plants. E. P. Partridge and A. L. Soderberg. (*Blast Furnace and Steel Plant*, 1942, vol. 30, June, pp. 664-670). The authors first discuss the prevention of deposits in boiler tubes and then deal with the problem of preventing the corrosion of steel by boiler water. For boilers working at under 250 lb. per sq. in. the accumulation of calcium-phosphate sludge can be reduced by organic dispersing agents such as tannin. In most cases, however, it is preferable to remove most of the calcium ion from the feed by primary softening, using phosphate within the boiler to clean up that passing the softener. Several references are made to the literature on the intergranular corrosion of boiler steel and the use of one of the direct forms of embrittlement testing is advocated.

Pulverized Coal for Forge Furnaces. R. B. Engdahl and F. E. Graves. (*American Society of Mechanical Engineers: Heat Treating and Forging*, 1942, vol. 28, July, pp. 327-330, 336-338; Aug., pp. 377-380, 400, 401). The authors report the results of tests on the possibilities of using pulverised coal for forging furnaces, which were carried out at the Battelle Memorial Institute.

Coal Washing—Its Effect on Coke Oven and Blast Furnace Practice. W. S. McAleer. (*Iron and Steel Engineer*, 1943, vol. 20, Jan., pp. 29-34). The author describes the characteristics of the Pittsburgh seam of coal and discusses the changes in ash and sulphur

content achieved by washing. Some data due to Seyler are quoted which show a marked improvement in blast-furnace operation at five plants as a result of using coke made from washed coal instead of coke from unwashed coal.

Influence of Storage on Caking and Coking Properties of Coal. L. D. Schmidt, J. L. Elder and J. D. Davis. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Feb., pp. 150-155). The authors describe an investigation, using 400-lb. samples from fifteen different American coal seams, in which these were oxidised progressively in an accelerated weathering apparatus and then subjected to a series of tests in order to follow the changes in their coking behaviour. The length of time the coals could withstand oxidising conditions before losing their coking power varied over a very wide range, some coals maintaining their coking power sixteen times as long as others. This maintenance of coking power can be predicted for most coals from the standard coal analysis ordinarily available before a coal is selected for storage. The effects of storage can be estimated by either the agglutinating-value test, or by examination of coke buttons made in the standard volatile-matter determination.

Coals for Byproduct Coking. J. D. Doherty. (American Gas Association: Coke and Smokeless-Fuel Age, 1943, vol. 5, Feb., pp. 28-33; Mar., pp. 49-52). The author reviews American practice in the mining and preparation of coals for coke-ovens with by-product recovery plants. Data on screen analyses, physical properties, and the ash, sulphur and moisture contents are presented. The value of such data and the results of expansion tests as a basis for the selection of coking coals are discussed.

The Heating of Coke Ovens. U. L. Koski. (Chicago District Blast Furnace and Coke Association: Blast Furnace and Steel Plant, 1942, vol. 30, July, pp. 775-777). The author describes the heating conditions of a coke-oven battery at the works of the Youngstown Sheet and Tube Co. The ovens were erected in 1928. Suggestions for improving the heating efficiency are made. Installing an exhaustor fan for induced draft would enable larger regenerators to be built. Such regenerators could be divided into two or three sections and, by having means of adjustment at the bottom of each and by not carrying the dividing walls to the top of the regenerator, it should be possible to control the flow of hot burnt gases through the checkerwork and to draw some of the hotter waste gases from the centre to the end of the regenerator, where the additional heat would be beneficial, since more heat is absorbed in the end flues.

Ammonium Sulphate Production. R. H. Nugent. (Chicago District Blast Furnace and Coke Association: Blast Furnace and Steel Plant, 1942, vol. 30, June, pp. 643-645). The author describes the production of ammonium sulphate at the works of the Youngstown Sheet and Tube Co. The raw gas is first passed through a

still to remove the tar; from this it is passed to reheaters to bring the temperature up to about 55° C., at which it enters the saturators. Inside the saturator, the gas is distributed by the cracker pipe into a sulphuric-acid bath. About 14.8 lb. of ammonium sulphate are produced per gallon of acid used, and the plant output is about 20 tons per day. The salt is dried in a rotary kiln 40 ft. long and 4 ft. in dia. Experiments on drying with infra-red rays are being made.

Foundry Coke from Blending of Southern Coals. W. M. Mobley. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Feb., pp. 148-150). The author proposes a standard specification for foundry coke which will satisfy the requirements of the average foundry. No coal in the Alabama coalfield when coked alone will produce a coke with the desired properties. The experience gained by one company in the selection and blending of coals for coking is related.

Physical Aspects of the Dust Catcher, Gas Washer and Precipitator on No. 3 Furnace at Carrie. C. P. Clingerman and C. J. Fleisch. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1533: Metals Technology, 1943, vol. 10, Jan.). The authors describe the recently installed gas-cleaning plant at the Carrie blast-furnaces of the Carnegie-Illinois Steel Corporation. It comprises a dust-catcher, gas-washer and precipitator. A radical departure from the use of 8-in. tubes in the Cottrell-type precipitators was made by constructing 12-in. tubes in a single compartment, the single compartment being divided into two units by a single partition wall in the top header. The results of some gas-cleanliness tests at various positions in the plant are presented. The degree of dust removal was much higher than that guaranteed.

PRODUCTION OF IRON

Republic Steel Operates New Blast Furnace. J. Stouffer and M. Morgan. (Iron and Steel Engineer, 1943, vol. 20, Jan., pp. 49-54). The authors give a comprehensive illustrated description of the 1100-tons-per-day blast-furnace which was blown in on Oct. 12, 1942, at the Youngstown Works of the Republic Steel Corporation. The hearth is 25 ft. 6 in. in dia., the bosh 28 ft. 3 in. in dia. The stack height is 107 ft. 3 in. and the working volume from tuyères to stock line is 40,100 cu. ft. All plate work on the furnace, stoves and gas-handling equipment is welded.

A New Technique in Blast Furnace Construction. (Blast Furnace and Steel Plant, 1942, vol. 30, Sept., pp. 995-996). A brief account is given of the manner in which a new blast-furnace was erected at the works of the Youngstown Sheet and Tube Co. The new

furnace, 100 ft. high and capable of producing 1050 tons per day, was constructed 104 ft. away from the old one while the latter was being dismantled. After the old foundations had been enlarged, the new furnace, weighing 600 tons, was moved bodily on rollers over heavy girders to the site occupied by the old one.

Blast Furnace for Production of Silvery Iron Has Novel Features. B. H. Booth. (Blast Furnace and Steel Plant, 1942, vol. 30, June, pp. 662-663). The author describes some features in the design of a new blast-furnace for making high-silicon silvery pig iron at the works of the Jackson Iron and Steel Co., Jackson, Ohio. The new furnace is built on the site of an old one, and the foundations had to be enlarged and strengthened. Instead of the columns resting on brick or concrete, they are securely riveted to a bed assembly consisting of eight members of 1½-in. boiler plate welded to form an octagonal foundation.

The Manufacture of Silvery Pig Iron by The Jackson Iron and Steel Company. B. H. Booth. (Blast Furnace and Steel Plant, 1942, vol. 30, Aug., pp. 877-880, 885-887, 923). The author describes how high-silicon pig iron is made at the new blast-furnace of the Jackson Iron and Steel Co. (see preceding abstract). Some locally mined coal is mixed with the coke fuel so as to attain the high temperatures required. The entire stack is water-cooled from the hearth jacket to the stock line. Slag control is not as important as working at a high temperature from the standpoint of sulphur elimination, but the silicon content depends on both factors. It takes about 12 hr. for a charge to pass through the furnace. Iron is tapped every 4-6 hr., the interval depending upon the silicon content required in the iron. The metal is tapped into a 65-ton covered ladle and is poured from this into the troughs of the pig casting machine. The cooling is closely controlled; very little water is used and the troughs travel slowly. Three slag tappings are made for each tapping of iron; the slag passes down a runner to a slag pit where it solidifies and is later dug out by steam shovel; it is then moved by rail to the slag plant where it is crushed, screened and sold for road construction and making concrete.

Blast Furnace Skip Hoist Operation with Amplidyne Exciter Control. C. P. Hamilton. (Blast Furnace and Steel Plant, 1942, vol. 30, Sept., pp. 1023-1025). The amplidyne exciter is a small D.C. generator with a special design of armature and field combination which gives the machine a high amplification factor between control input and power output, and a very quick response to the controlling sources. A blast-furnace skip-hoist installation is described in which the winding drum is driven by two shunt-wound, 150-h.p. motors, each motor armature in turn being electrically connected to an individual generator excited by an amplidyne.

Mercury-Arc Rectifier Vs. Motor Generator. L. R. Milburn. (Iron and Steel Engineer, 1942, vol. 19, Dec., pp. 28-36). The author describes how mercury-arc rectifiers were applied at the

Detroit plant of the Great Lakes Steel Corporation to supply additional direct current for the new sintering plant, blast-drying machinery and ore-bridge cranes.

Results Obtained from Surveys of Gas at Furnace Tops. J. M. Stapleton. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1541: Metals Technology, 1943, vol. 10, Jan.). The author describes equipment which was installed at the top of two blast-furnaces at the South Works of the Carnegie-Illinois Steel Corporation in order to draw off top-gas samples at distances of 6 in., 2 ft., 4 ft., 5 ft. 6 in., 7 ft. 6 in. and 9 ft. from the furnace wall on a plane 8 ft. below the bottom of the large bell. Data on the CO/CO_2 ratio in many series of samples are presented, and these are related to the conditions of furnace operation. The conclusions reached include: (1) Gas sampling in the manner described indicates how the distribution of the materials at the top affects the flow of gas and it often indicates changes in charging practice which should be made. (2) Furnaces operating efficiently have a low CO/CO_2 ratio in the gas near the furnace wall. (3) Temperature readings are a guide to the CO/CO_2 ratios. (4) Single traverses in sampling may indicate trends caused by changes in charging practice, but several traverses should be made before final conclusions are drawn. (5) Furnaces of similar dimensions, operating under similar conditions, but differing widely in performance can sometimes be brought into line by some simple adjustment the nature of which having been determined by traverse gas sampling.

Blast Furnace Tapping Holes. L. Tofft. (Chicago District Blast Furnace and Coke Association: Blast Furnace and Steel Plant, 1942, vol. 30, Aug., pp. 892-894, 923; Sept., pp. 1010-1015). The author describes investigations at the blast-furnaces of the Inland Steel Co., the object being to establish the best practice in drilling and closing tap holes using an electrically driven dolly and clay gun. Data were obtained on the effects of changing the tap-hole angle, the rate at which the clay is put in, the volume of clay used and the blast pressure. Good results were obtained by stopping the hole with one stroke of the dolly and by checking the furnace before the end of the cast. A change in the drilling angle may improve the casting characteristics of the furnace, but it does not necessarily change the hole length. There is an optimum amount of clay to stop the hole for each furnace, which enables successive tap holes to be maintained over a long period at a length approximately equal to the original wall thickness.

Slag Control by Introduction of Flux through Blast-Furnace Tuyères. C. G. Hogberg. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1523: Metals Technology, 1943, vol. 10, Jan.). Under war-time conditions coke for blast-furnaces is drawn from a large number of sources, its ash content varies, and this affects the properties of the blast-furnace

slag. The author suggests that under these conditions better slag control could be obtained by blowing some of the lime into the furnace through the tuyères and reducing the amount charged through the top of the furnace. He refers to G. E. Steudel's paper on bosh and hearth slags (see Journ. I. and S.I., 1940, No. I., p. 7 A), presents data on the effect of variations in coke ash on the hearth slag analysis and calculates the amounts of lime that would be required for different percentages of coke ash to produce a slag of given composition and melting point. If the lime were injected immediately after tapping, the higher-lime slag would tend to stratify immediately above the metal bath in the hearth and might prove much more effective as a desulphuriser than the more acid slag formed as the siliceous oxides from the coke ash progressively dilute the slag during the smelting period.

Dangers of Explosion and Poisoning in the Crushing of Ferro-Manganese. Bauer and Hagen. **A Note on the Crushing of Ferro-Manganese.** Mátray. **A Note on Mátray's Report.** Bauer. (Iron and Steel Institute, 1943, Translation Series, No. 137). This is an English translation of three publications which appeared in 1942 in the *Reichsarbeitsblatt*, the first one in Part III., No. 8, the two following ones in Part III., No. 23. In the first paper the authors describe in detail the practice at a works where ferro-manganese produced in an electric furnace is crushed. In 1941 a violent explosion occurred in the crushing plant, and the possible causes of this are discussed. They report also on five serious cases of manganese poisoning, which occurred in the same plant. In conclusion they make a number of suggestions by which the danger of explosion and poisoning in ferro-manganese crushing plants is minimised. The author of the second paper reports on the experience gained at a Budapest works in which ferro-manganese required for coated electrodes is disintegrated in jaw and roller crushers and in a beater mill with special ancillary equipment. No serious difficulties were experienced when crushing ferro-manganese, whereas when metallic manganese was treated in the same plant it caught fire. The last communication consists largely of comments on the second one, the possible dangers of treating ferro-manganese in a beater mill being emphasised.

The Reduction of Iron Ore under Pressure. (Stahl und Eisen, 1943, vol. 63, Mar. 4, p. 180). A brief account is given of some experiments by E. Edwin on the production of sponge iron under pressure. In order to fix the carbon dioxide produced when reducing iron ore with carbon, burnt lime is added; the process temperature is about 900° C., but it is necessary to carry out the reduction under a pressure sufficiently high to overcome the dissociation of the limestone; at 900° C. a pressure of about 25 ats. is required. Whilst it is a disadvantage that the process is under pressure, there is on the other hand the advantage that a considerable amount of heat is released by the reaction of carbon dioxide with lime. Labora-

tory tests at Krupps works with 4 kg. of ore, lime and coke in an electrically heated autoclave resulted in 95% of the oxygen being removed in 4 hr. but the ore, lime and coke ash had not reacted with each other and were left in the form of easily separated powders. In this test, after heating up to 950° C., the current was reduced to an amount sufficient to balance the external heat loss. In another trial with a 1-ton charge in a rotating pressure vessel, 90% reduction was achieved, but the rotation had some detrimental effects, in that the charge tended to separate itself into layers according to weight. From the experience gained plans have been drawn up for a vertical reduction furnace, suitable for Norwegian conditions, which will use some of the surplus gas from electric furnaces producing pig iron.

Synthetic Scrap by Direct Reduction. E. S. Harman. (Iron and Steel Engineer, 1943, vol. 20, Jan., pp. 66-74). The author gives a detailed description of the Harman process and plant for producing direct from ore a metal in the form of either sinter or pig which is suitable for charging in steel furnaces. The plant described has a capacity of 400 tons of this "synthetic scrap" per day from an ore containing 50% of iron. Ore, limestone and carbon in the form of coal, coke or oil coke in the proportions 40/8/5 are dried, crushed to about $\frac{1}{16}$ in., intimately mixed and fed into the upper end of a sloping rotary kiln. As the material advances through the kiln it is heated by a reducing atmosphere, the solid carbon in the charge reducing the ore; in this stage of the process there is no excess of carbon to reduce the silica in the ore, which combines with calcium in the limestone to form silicates. Further down the kiln the material is impregnated with additional carbon, sintered and then discharged into a vertical cylindrical melting furnace. The carbon in the product is controlled by carbon additions made directly to the metal below the slag in the melting furnace. The slag in this furnace is basic with a lime content of 40% or over. The sinter falls through a short shaft 7 ft. 6 in. in dia. into the centre of the bath, which is 20 ft. in dia., in which a reservoir of about 18 in. of metal is maintained at all times. A certain amount of iron oxide is carried into the furnace from the kiln, and to reduce that which is in the slag a carbon-monoxide flame is maintained above the slag by twelve burners; there are another twelve burners above these, the latter producing a slightly oxidising flame. Above these is still another series of burners, through which incandescent pulverised coke is injected to reduce the carbon dioxide in the exit gases to carbon monoxide. The fuel equipment includes two recuperators and plant for distilling the volatile gases coming from the heated pulverised coal as it passes through the recuperator plates.

Powder Metallurgy: Its Products and Their Applications. W. D. Jones. (North-East Coast Institution of Engineers and Shipbuilders: Metallurgia, 1943, vol. 27, Mar., pp. 185-187, 194). The author describes how tungsten-carbide tools, electrical contact

materials, Alnico magnets and tungsten wire are made by powder metallurgy. In iron articles made by this process, a tensile strength of up to 25 tons per sq. in. presents no difficulty in production.

Powder Metallurgy. J. Wulff. (American Society for Metals: Canadian Metals and Metallurgical Industries, 1943, vol. 6, Feb., pp. 30, 42). The author discusses some technical aspects of powder metallurgy. Some of the effects of changes in temperature and time when compressing iron powders are mentioned. At 450° C. in a reducing atmosphere no improvement in structure was obtained until 4 hr. had elapsed, whilst better results were obtained in much less time at 500–550° C.

The Present Position of Powder Metallurgy. R. Kieffer and W. Hotop. (Iron and Steel Institute, 1943, Translation Series, No. 133). An English translation is presented of a paper which appeared in *Stahl und Eisen*, 1940, vol. 60, June 13, pp. 517–527. See *Journ. I. and S.I.*, 1941, No. II., p. 163 A.

FOUNDRY PRACTICE

Ironfounding in Australia. H. Dalziel. (Institute of Australian Foundrymen: Foundry Trade Journal, 1943, vol. 69, Feb. 25, pp. 161–164, 168; Mar. 4, pp. 181–185). The author presents a comprehensive survey of current practice in ironfounding in the Australian Commonwealth. Normally there are available some 38 grades of pig iron, classified as "Standard" and "Special," the former with phosphorus up to 0.30%, whilst the latter are high-phosphorus irons with 0.6–0.9%. Various silicon contents can be obtained up to 4.5%. Inoculated and alloy irons are being used to an increasing extent.

Design as Related to Casting Problems. E. B. Carpenter. (American Foundrymen's Association: American Foundryman, 1942, vol. 4, Dec., pp. 1–6). The author describes and illustrates several examples of improvements in the design of castings which have helped to overcome moulding and other difficulties in the foundry.

Desulphurizing of Cast Iron. G. S. Evans. (Metals and Alloys, 1942, vol. 16, Nov., pp. 876–880). The author discusses the reactions between the sulphur and impurities in iron and soda ash and caustic soda, and describes methods of adding these desulphurisers and the form in which they are available.

Foundry Techniques in Relation to Certain Pressure Castings. F. Dunleavy. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 69, Mar. 18, pp. 217–221; Mar. 25, pp. 239–242, 244). The author describes and illustrates how certain types of castings are made at the foundry with which he is connected. The castings include small impellers of grey iron, air-compressor

cylinders and crankcases, pump casings and a grey-iron evaporator body weighing about 6 tons.

Graphitisation of Martensite on Heating. A. Hultgren and O. Edström. (Iron and Steel Institute, 1943, Translation Series, No. 134). This is an English translation of a paper which appeared in *Jernkontorets Annaler*, 1942, vol. 126, No. 3, pp. 83-107 on an investigation of the effect of prehardening on the formation of graphite nuclei in cast iron on malleableising it, the object being to shorten the time required for malleableising (see *Journ. I. and S.I.*, 1943, No. I., p. 122 A).

PRODUCTION OF STEEL

Developments in the Iron and Steel Industry during 1942. W. H. Burr. (*Iron and Steel Engineer*, 1943, vol. 20, Jan., pp. 76-95). The author reviews developments in the iron and steel industry of the United States which have taken place during 1942.

Film Refining Process of Steelmaking. J. M. Merle. (*Steel*, 1942, vol. 111, Dec. 14, pp. 92-96, 131; Dec. 21, pp. 84-87, 109-111). The author describes a continuous process of steelmaking and the necessary equipment. In this process separately produced molten iron and a refining slag are simultaneously fed into a revolving refractory-lined chamber. The intimate mixing of the two materials and the fact that the contact surface is very large in proportion to the volume cause the refining reactions to take place exceedingly rapidly. As the molten metal within the chamber at any given time forms a layer only about $\frac{3}{16}$ in. thick against the refractory lining, the process is called the "Merle film-refining process." These rotary refiners are made in different sizes to produce from 1 to 3 tons of steel per min. It is claimed that the method permits of much closer control than either Bessemer-converter or open-hearth refining, and that it is more convenient to have the steel available continuously than it is to have heats of 100-200 tons ready all at once.

Factors Affecting the Design of O.-H. Furnaces. A. H. Leckie. (*Lincolnshire Iron and Steel Institute: Iron and Coal Trades Review*, 1943, vol. 146, Mar. 26, pp. 451-455). The author discusses some of the principles applied in the calculation of the flow of fuel gas, air and waste gas entering and leaving open-hearth furnaces, the determination of furnace pressure balances, checker design and furnace design. The steps leading to efficient furnace design from the aerodynamic point of view comprise: (1) Calculate the gas, air and waste gas flow. (2) Choose the maximum convenient dimensions for the various passages and construct the pressure balance for air, gas and waste gases. From these it will be

seen whether the available gas pressure will be adequate, whether positive air will be necessary and what draft will be required. The necessity for any modifications in the dimensions of the passages will be revealed. (3) During the first few campaigns it should be possible to obtain a good idea of the best port design and dimensions for this type of furnace from the characteristic curves. The special problem of large tilting furnaces is dealt with.

The Utilisation of Phosphatic Open-Hearth Slag. Part I. Effect of Rapid Cooling on the Solubility of Phosphoric Acid. F. E. Lathe. (Journal of the Society of Chemical Industry, 1943, vol. 62, Feb., pp. 24-28). The author reviews the literature and reports the results of recent investigations on the use in agriculture of open-hearth slag produced at Sydney, Nova Scotia, by the Dominion Steel and Coal Corporation (Dosco). Granulation of "run-off" slags by water-quenching resulted in considerably higher citric-acid solubility of the contained phosphate than occurs in air-cooled slag. With "tapping" slag the effect of granulation was similar, but much smaller. Granulation facilitated removal of part of the iron prior to crushing and grinding the slag.

The Utilisation of Phosphatic Open-Hearth Slag. Part II. The Availability of Phosphoric Acid as Measured by Yield and Phosphorus Recovery in Barley and Clover. L. E. Wright, A. Leahey and R. C. Turner. (Journal of the Society of Chemical Industry, 1943, vol. 62, Feb., pp. 28-31). The authors report the results of a greenhouse experiment using soils from two experimental farms in Nova Scotia to compare the availability of the phosphoric acid in Dosco open-hearth slag (*see* preceding abstract). The granulated slags gave higher yields than the corresponding air-cooled slags in all cases, except with clover from one soil for which very little difference was apparent. The differences were not always statistically significant. The "tapping" slags gave better yields of clover than the "run-off" slags where no calcium carbonate was applied to the soil.

First Helper's Hand Book of Slag Control. J. T. Mauer. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1942, vol. 30, June, pp. 656-660). The author explains, in a manner suitable to be a guide to the first helper, the reactions governing the formation and control of the slag in basic open-hearth furnace operation. The procedure for taking slag samples and estimating the lime/silica ratio from their appearance is described.

The Preparation and Use of Iron Ores for High Hot-Metal Heats. R. W. Tindula. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1942, vol. 30, July, pp. 763-768). The author discusses the desirable properties of iron ores for the basic open-hearth process, using charges with a high proportion of hot metal and a minimum of steel scrap. With magnetite ores a coarse sinter gives much better results than

medium and fine concentrates, but with hematite ores there is little difference in the results obtained with coarse and fine ores.

Experiences with Arc-Furnace Roofs of Standard Bricks with Built-In Metal Cooling Collars. H. Müller. (Stahl und Eisen, 1943, vol. 63, Mar. 18, pp. 217-220). After discussing the attempts which have been made to improve the life of electric-arc furnace roofs built of silica bricks and requiring many special shapes of brick, the author describes a roof design for 15-20-ton furnaces which can be built almost exclusively of standard square bricks. This design makes provision for three metal cooling collars, one surrounding each electrode, suspended from two parallel bearers spanning the whole furnace. This design of roof has been used for 16 years. Improvements have been made during this period and a considerable decrease in the consumption of roof bricks per ton of steel has been achieved.

The Removal and Taking-Up of Nitrogen in Steel Baths in the Basic Arc Furnace. W. Altpeter. (Iron and Steel Institute, 1943, Translation Series, No. 136). This is an English translation of a paper which appeared in Stahl und Eisen, 1942, vol. 62, Nov. 26, pp. 997-1001. See Journ. I. and S.I., 1943, No. I., p. 156 A.

A Method for the Control of Electric Arc Furnaces. T. B. Montgomery. (Blast Furnace and Steel Plant, 1942, vol. 30, Aug., pp. 861-868). The author considers the requirements of the control equipment for an electric-arc furnace and describes a suitable circuit and control panel.

Electric Arc Hot Topping. G. F. Sullivan. (Iron Age, 1943, vol. 151, Feb. 11, pp. 56-60). The author reports and discusses the results of examinations of ingots the tops of which were kept hot by the application of an electric arc from a carbon electrode. At one works the process was applied to 8-in.-square ingots; the electrode consumption was 8 oz. per ton of ingot and the power consumption 14 kWh. per ton of ingot. In this case it was possible to work the entire ingot without cropping; with stainless steel the flat upper surface of the ingot opened slightly during forging, but the amount of cropping necessary was less than 5%. At a Pittsburgh foundry the process was successfully applied to the vertical casting of large rolls for rolling mills. A dome-shaped roof of moulding sand with a hole in the centre was placed over the mould top after pouring, and the electrode was lowered through the hole; the circuit was completed through an iron bar thrust into the top of the riser while still molten. Without using the arc, a roll 40 in. in dia., 133 in. long, weighing about 23 tons required a riser 36½ in. in dia., 60 in. long, weighing 63% of the weight of the roll. Using the arc, the weight of the riser was reduced to 31% of the weight of the roll; the power consumption was about 24 kWh. per ton of metal poured.

FORGING, STAMPING AND DRAWING

Compressed Air for Forge Hammers. J. M. Weil and P. Hoffman. (Compressed Air Institute: Heat Treating and Forging, 1942, vol. 28, Sept., pp. 519-521). The authors compare the efficiencies of compressed-air and steam forge hammers. The unavoidable disadvantages of steam-driven hammers include: (a) The hammer cylinder uses steam most uneconomically; (b) a hammer cylinder is subject to severe heat losses which cause heavy condensation; (c) the condensation in turn causes poor lubrication, rapid cylinder and piston-ring wear and high maintenance charges; and (d) as most forge shops operate with a poor load-factor, the boiler plant usually has high stand-by losses. When a steam-operated hammer is converted for use with compressed air, the practice of idle oscillations, which is standard for steam to blow condensate out of the cylinder, is generally allowed to continue with the compressed-air operation. This is a serious mistake, for it has been found that the air consumption during idle oscillations is 50% or more of that during the working cycle. Time studies have shown that, over a working day, $1\frac{1}{2}$ times as much air is used in idling as for actual productive work. Compressed-air power is more economical than steam for a forge shop equipped mainly with impression-die drop hammers.

Forging and Welding 1000-lb. Aerial Bombs. J. B. Nealey. (Iron Age, 1943, vol. 151, Feb. 11, pp. 49-54). The author describes and illustrates a method of manufacturing 1000-lb. bomb-cases from seamless steel tubing in which the nose and tail ends are hot-formed and machined separately and are then welded together.

The Forging of Edged Tools. C. F. Forstall. (Heat Treating and Forging, 1943, vol. 29, Jan., pp. 17-20). The author describes the forging machinery and processes used in the manufacture of picks, wedges, hoes and crowbars.

The Transition Radii of the Walls of Forgings. P. Patek. (Heat Treating and Forging, 1942, vol. 28, June, pp. 275, 300). The author discusses and presents formulæ for calculating the optimum radii at the angles in pressing dies.

Proper Location of the Burr on Forgings. P. Patek. (Heat Treating and Forging, 1942, vol. 28, July, pp. 331-332, 344). The author discusses factors affecting the position and contour of that portion of a pair of forging dies into which the burr or fin of surplus metal is forced. He explains how to calculate the burr length and thickness from the point of view of obtaining the best cooling rates.

Determination of the Initial Material for a Forging. P. Patek. (Heat Treating and Forging, 1942, vol. 28, Aug., pp. 381-382, 401-403). The author presents formulæ and explains their application for calculating the dimensions of the initial material for a forging so as to include allowances for machining, shrinkage of the

cooling steel after removal from the die press, waste arising from scale and burr formation.

The Volume of Hollow Grooves and Punch Points. P. Patek. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 525-527). As a supplement to the information on calculating the volume of initial material required for a forging made between closed dies (*see* preceding abstract), the author shows how to calculate the increase in the volume of metal arising when the radius at the root of the angle between two faces of a forging exceeds 3 mm. as well as that due to the radius of the punch point in the male die.

Drawing and Indenting Simultaneously. C. W. Hinman. (Heat Treating and Forging, 1942, vol. 28, June, pp. 280-281). The author describes a pair of dies for pressing sheet metal box covers and at the same time making an indent in the rim on one of the four sides.

Dies for Double-Action Presses. C. W. Hinman. (Heat Treating and Forging, 1942, vol. 28, July, pp. 340-342). The author describes the design of a pair of dies for making troughs in a double-action press in which the outer ram acts as a holder for the blank and the centre ram carries the drawing and forming punch.

Roll Feeds and Automatic Stops. C. W. Hinman. (Heat Treating and Forging, 1942, vol. 28, Aug., pp. 384-385). The author describes a simple form of feeding-roll equipment for feeding strip into a high-speed punching press. A friction grip is incorporated which prevents sudden jolts when the strip is brought to rest for blanking.

A Three-Way Adjustable Die. C. W. Hinman. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 479-481). The author describes the design of an adjustable die for making brackets for wireless sets out of steel strip $\frac{1}{2}$ in. wide and $\frac{1}{16}$ in. thick. The die was adjustable in that any one of eighteen different lengths of bracket with punched holes at different pitches could be produced with it.

A Progressive Die for Tubular Work. C. W. Hinman. (Heat Treating and Forging, 1943, vol. 29, Jan., pp. 26-28). The author describes the design of dies for the mass production of short lengths of tube separators or tubes of unsymmetrical cross-section.

Notes on Shell Forging. J. B. Nealey. (Machinist, 1943, vol. 86, Mar. 20, Armament Section). The author discusses the advantages and disadvantages of the pierce-and-draw and upsetter methods of producing shell forgings and describes a gas-fired, rotary-hearth billet furnace with a suspended flat roof, a circular refractory section in the centre and an annular heating space. This is capable of heating over 4000 shell billets, 105 mm. in dia., to 2240° F. every 24 hr. From this furnace the billets pass on a roller conveyor to a high-pressure spray for descaling, and thence to a vertical Ehrhardt piercing press. The down stroke of the press, when piercing 105-mm. shell, is accomplished in about 4 sec. The forged shells are lengthened and narrowed by pushing them through

a series of three annular ring-type dies. Quenching of this high-sulphur steel is accomplished inside a 16-in. dia. pipe about 30 ft. long by a current of air forced through by blowers.

Upsetting—Its Principles and Practice. J. Mueller. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 472-473; Oct., pp. 522-524; Dec., pp. 631-632, 646). The author makes recommendations for upsetting practice, describing the "ball and gather" and progressive taper methods, and discussing the design of dies, punches, punch holders and the maintenance of upsetting machines.

Steel and Wire. L. H. Winkler. (Mordica Memorial Lecture: Wire and Wire Products, 1943, vol. 18, Jan., pp. 17-32). The author presents a review of all the processes involved in wire-making from the smelting of ore in the blast-furnace to the manner in which the desired properties in the finished wire are obtained by various methods in the wire mill.

ROLLING-MILL PRACTICE

Special Applications of Steel Plant Control. H. H. Angel. (Iron and Steel Engineer, 1942, vol. 19, Dec., pp. 50-52). The author describes some special methods of electrical control which were developed by the Bethlehem Steel Co. in order to: (a) improve the operation of a 10-ton crane for charging slabs into a reheating furnace; (b) improve the division between three generators of the load required by mill motors; and (c) improve the speed control of a motor driving a steel strip coiler.

Developments in Control Equipment and Devices. E. H. Alexander. (Iron and Steel Engineer, 1942, vol. 19, Dec., pp. 56-63). The author reviews improvements in the following types of electrical control equipment: (1) High-voltage A.C. control; (2) low-voltage A.C. control; (3) D.C. control and accessories; and (4) electronic control.

Maintenance of Insulating Oils. R. P. Dunmire. (Iron and Steel Engineer, 1942, vol. 19, Dec., pp. 42-48). The author discusses the properties and the effects of moisture and impurities on insulating oils used for transformers, circuit breakers and oil-filled cables. Examples of specifications for transformer oils are given and the "hydrovolifier" process of purifying oils is described. This process is a form of low-temperature vacuum distillation in a portable plant which removes the water and lighter hydrocarbons in a purely physical manner without any chemical treatment.

Rolling-Mill Bearings of Wood Impregnated with Synthetic Resin. S. Hellmanns and E. Rohde. (Stahl und Eisen, 1943, vol. 63, Mar. 18, pp. 209-216). The author describes the development in Germany of a material for rolling-mill bearings made of synthetic resin reinforced with layers of beechwood. This material

has been found to give better service than synthetic resins with textile reinforcement. The design of the bearings is discussed.

The Synthetic Resin Bearings of the Largest Rolling Mill in the World. J. Arens. (Kunststoffe, 1942, vol. 32, Aug., pp. 237-241). The author gives details of the design of the synthetic resin bearings for an armour-plate rolling mill. The mill stand has two backing rolls and two working rolls 1600 mm. and 1100 mm. in dia. respectively, and is capable of rolling slabs of up to 165 tons (see Journ. I. and S.I., 1942, No. I., p. 232 A). The bearings are lubricated with extreme-pressure grease and cooled with water. The experience gained after some months working of the new mill confirms the superiority of these bearings over non-ferrous metal bearings.

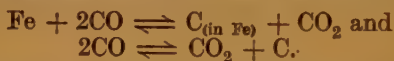
The Distribution of Forces in Rolling. F. Holmberg. (Teknisk Tidskrift, 1943, vol. 73, Jan. 9, pp. B1-B3). (In Swedish). In this mathematical treatise a simplified formula is developed which represents, with sufficient accuracy for practical purposes, the actual distribution of forces in the rolling of plates and ingots.

Active Pass Contours in Wide Strip Rolling. W. J. Blenko. (Blast Furnace and Steel Plant, 1942, vol. 30, June, pp. 649-655, 661). The author reports the results of investigations at several continuous wide strip-mills, the purpose of which was to test the validity of the theory that the contour of the sheet leaving each stand must be of progressively decreasing convexity. The procedure adopted was to obtain standard rolling conditions for the particular mill and cut a test-piece across the trailing end of the strip as it left the last stand. The upper working roll of the last stand was lifted and the guides were separated; another strip was run through the mill and a test-piece cut from this as it left the penultimate stand. This procedure was repeated by lifting the rolls of successive stands and the convexity of each test strip was measured. The conclusions reached were: (1) It is not essential to the successful rolling of wide strip in continuous four-high mills for the passes to have progressively decreasing convexity; (2) as long as the contour is substantially symmetrical about the centre line of the strip, the strip will "track" satisfactorily through the mill; (3) if the reduction is not proportional across the width of the strip, transverse flow of the metal occurs; (4) there are material deviations in thickness at the edges, due to local action of the rolls, and data on strip contours should take account of this; and (5) the data obtained and the conclusions drawn apply to four-high stands only.

HEAT TREATMENT

Fundamentals of Good Carburization. J. K. Stanley. (Metal Progress, 1942, vol. 42, Nov., pp. 849-855). The author considers
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the theory of factors affecting the most important of the reactions occurring in the case-hardening of steel, namely :



Tables and graphs are presented showing the percentage composition and partial pressure of each gas in CO-CO₂ mixtures at equilibrium and how these are affected by changes in temperature and pressure and by the presence of moisture and of carbon in the steel. It is shown how the curves can be used to determine the behaviour of steel in different atmospheres under various conditions.

Steel Carburization and Decarburization—A Theoretical Analysis.

J. K. Stanley. (Iron Age, 1943, vol. 151, Jan. 21, pp. 31-35; Jan. 28, pp. 36-39; Feb. 4, pp. 49-55). In the first part of this series of articles on the theory of carburisation and decarburisation, the author shows how to determine the equilibrium constant for the carbon-monoxide/iron system, and discusses how its value is affected by temperature and pressure. In the second part the theory of reactions between iron and methane-hydrogen mixtures and the decarburisation by carbon dioxide, oxygen or air, and moisture are explained. In the concluding part the effects of time, temperature and grain size on the depth and rate of carburising are considered.

The Flame Hardening Process. (Machinery, 1943, vol. 62, Apr. 8, pp. 365-370). After a general discussion of the flame-hardening process a description is given of a flame-hardening machine fitted with two pairs of oxy-acetylene burners and quenching jets so arranged that both sides of a gear-tooth are traversed simultaneously. Micrographs of gear teeth hardened in this way are reproduced.

New Developments in Flame Hardening. S. Smith. (Welding Journal, 1943, vol. 22, Jan., pp. 21-23). The author describes the development of flame hardening as applied to the surface of rails. The latest form of equipment comprises a standard multi-flame oxy-acetylene burner head followed by a quenching jet, which in turn is followed by a shield and a second, less powerful, multi-flame head to supply the tempering heat at the desired distance behind the quenching jet; all these components are fixed to one bracket, which is moved along the top of the rail.

Unusual Nitriding Furnace for Heavy Parts. W. F. Ross. (Heat Treating and Forging, 1942, vol. 28, July, pp. 347-349). The author describes an installation of nitriding furnaces of the vertical cylindrical type. The charge is assembled upon the furnace support stool, an open cylindrical baffle is lowered over it, and over the latter a bell-shaped retort is put in position with its open end resting in an annular trough containing oil to act as a seal. Ammonia gas is passed through permanent pipe connections in the furnace base. A fan under the stool provides for forced

circulation of the ammonia, which passes up beside the wall of the bell, over the top of the open-ended baffle and downwards over the charge. Heat is provided by passing the gases from an external gas-fired combustion chamber between the double walls of the bell.

The Behaviour of S.82 about its Critical Range, and the Application of this to Annealing Practice. C. Wilshaw. (*Metallurgia*, 1943, vol. 27, Mar., pp. 191-194). The author explains the structures produced in specimens of carburised S.82 steel (carbon 0.21%, manganese 0.45%, nickel 4.00%, chromium 1.17%) after soaking for different periods and oil-quenching from different temperatures in the 600-800° C. range, and describes a method of annealing this steel in the carburised state at 680° C. to facilitate machining.

The Heat Treatment of Large Shafts. (*Heat Treating and Forging*, 1942, vol. 28, Aug., pp. 373-375; Sept., pp. 543-547). Reference is made to a trouble known as the "rough running" of turbine shafts, which develops although initially the shaft is correctly centred and properly finished to the dimensions specified. This has been traced to the fact that the distribution of the grain size, and possibly other physical values, are not symmetrical to the axis of rotation. Two patented methods of preventing this are described, one due to H. J. Stein and the other to S. H. Weaver. Both methods are based on rotating the ingot in the forging furnace, and the shaft in the heat-treatment furnace, so as to ensure that the heat penetrates concentrically towards the longitudinal axis.

Bright Annealing Protective Atmospheres. (*Brown-Boveri Review: Iron and Coal Trades Review*, 1943, vol. 146, Apr. 16, pp. 565-567). A description is given of a charcoal-gas producer developed by Brown-Boveri with which bright annealing protective atmospheres of controlled composition can be obtained. A mixture of carbon monoxide and carbon dioxide is generated in a gas producer, and this mixture is led through an electrically heated container filled with charcoal. The temperature of the charcoal is maintained constant automatically, and depends on the desired carbon-monoxide content. The mixture is drawn through a second container provided with baffle plates, where it is cooled down and gives up moisture and dust. A sealed charcoal-charging receptacle is placed above the producer. The consumption of charcoal is extremely low, and fluctuates, according to the carbon-monoxide content of the atmosphere produced, between 100 and 160 g. per cu. m. of gas.

Spheroidize Annealing of S.A.E. 52100 Steel. R. J. Hafsten. (*Metal Progress*, 1942, vol. 42, Nov., pp. 869-873). The author describes an investigation of ball-bearing steel S.A.E. 52100 to determine the heat-treatment conditions under which the austenite ceases to deposit spheroidal carbide and begins to form pearlite. The specimens tested contained carbon 1.04%, manganese 0.45%, silicon 0.34%, nickel 0.13% and chromium 1.44%. Specimens

were heated for 1 hr. at 1430° and at 1500° F., held in molten lead for 2 hr. at various temperatures in the 1360–1260° F. range, and finally quenched in water. The steel converted to austenite at 1430° F. transformed directly to spheroidal carbide at temperatures from 1275° to 1340° F. After 2 hr. at 1360° F. no transformation had taken place. Pearlite made its appearance at somewhere between 1275° and 1260° F. From this it was deduced that a spheroidised structure could be obtained very economically in a continuous furnace having two or more zones with independent temperature control to each. The size of the cementite spheroids depends on the time for which the steel is held at below the critical temperature. The rate of cooling from the upper temperature to the critical temperature does not influence the structure formed at below the critical temperature.

Metallurgical Factors in Forming and Heat Treating Cartridge Links. (Heat Treating and Forging, 1942, vol. 28, Aug., pp. 386–389, 395). A description is given of the heat-treatment operations in the manufacture, at mass-production rates, of loop links to form belts to carry 0.50-in. machine-gun ammunition. The material used is cold-rolled annealed strip steel containing 0.59–0.74% of carbon.

The History of Double Hardening. E. Maurer. (Stahl und Eisen, 1943, vol. 63, Mar. 11, pp. 200–201). The author studies some early patents relating to the heat treatment of steel by hardening and tempering and gives details of some tests made by Walrand and Cottin at Creusot in 1880.

A Metallurgical Study of Some NE (National Emergency) Alloy Steels. T. A. Frischman. (Steel, 1942, vol. 111, Dec. 14, pp. 99, 119–123). The author discusses and gives information on the response to heat treatment of some of the 8000-series of National Emergency steels.

Heating and Forging Operations in Maintenance of Railroad Rolling Stock. C. Cleveland. (Heat Treating and Forging, 1942, vol. 28, June, pp. 271–274, 287). The author gives an illustrated description of the heat-treatment furnaces and equipment for making springs for the rolling stock of the Pennsylvania Railroad.

Heat-Treating Practice at the Cleveland Hardware and Forging Company. J. Mueller. (Heat Treating and Forging, 1942, vol. 28, Aug., pp. 391–393). The author describes the furnaces and procedure for the heat treatment of small parts in trays at the works of the Cleveland Hardware and Forging Co., Ohio.

Heat Treatment of Small Arms Parts. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, Jan., pp. 2–5). An illustrated description is given of the heat-treatment plant and processes for small-arms parts at the works of the John Inglis Co. in Canada.

Heat Treatment of Gun Tubes. (Heat Treating and Forging, 1942, vol. 28, July, pp. 350–351). The heat-treatment processes to which forgings for 37-mm. and 75-mm. guns are subjected are described.

Modern Heat-Treating Plant Equipped for Complete Service to War Industries. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 491-492). A brief description is given of a modern heat-treatment plant set up in Texas in 1936 by the Cook Heat-Treating Corporation. The plant comprises six Mahr gas-fired hardening furnaces, two Lindberg Cyclone furnaces, one Leeds and Northrup gas-carburising furnace and two salt-bath carburising furnaces together with some smaller electric furnaces for tools and dies.

Heat Treating Furnaces—Types Used in Production of Munitions of War. R. J. Cowan. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 485-487; Oct., pp. 541-542). The author describes and illustrates the following types of heat-treatment furnaces which are now being extensively used for munition production: (1) Pit-carburising furnaces; (2) pit-hardening furnaces; (3) roller-hearth furnaces; (4) continuous gas-carburising furnaces; and (5) conveyor-belt hardening furnaces.

Automatic Units for Heat Treating High-Explosive Shells. D. H. Gardner and J. Wallerius. (Metal Progress, 1942, vol. 42, Nov., pp. 861-866). The authors describe a fully automatic unit for the continuous heat treatment of shell forgings in the rough-machined state. The unit consists of a hardening furnace through which six rows of shells pass along six parallel slotted tubes of 12/27 chromium-nickel steel. The shells are moved by a pusher at timed intervals. At the discharge end each shell passes into a quench cage and descends a sloping chute into the oil-bath. The shells are also quenched internally by an oil-jet. They are next mechanically tipped over on to a conveyor, which withdraws them, base first, from the oil and delivers them to the tempering furnace, through which they pass on a chain conveyor to the cooling chamber.

Martempering. B. F. Shepherd. (Iron Age, 1943, vol. 151, Jan. 28, pp. 50-52; Feb. 4, pp. 45-48). The author explains a method of quenching steel the object of which is to prevent distortion and residual stresses. It is based on a knowledge of the temperatures at which the beginning and end of the transformation to martensite for the steel in question occur. A quenching medium, usually a bath of molten salts, is selected such that there is a minimum temperature difference between the outside and centre of the part when the outside reaches the temperature at which martensite begins to form. The part is held in the bath sufficiently long for its temperature to become uniform, after which it is cooled in air. Depending on the composition and size of the part, it may be desirable to initiate a fast cooling rate by a short-time quench in oil or brine immediately followed by holding in the molten salts to obtain uniform temperature across the part, and finally cooling in air. Data on the cooling rates and hardness of round bars of some of the National Emergency steels in baths at various temperatures are presented.

WELDING AND CUTTING

Physics of the Arc and the Transfer of Metal in Arc Welding. W. Spraragen and B. A. Lengyel. (Welding Journal, 1943, vol. 22, Jan., pp. 2-S-42-S). The authors present a review of the literature to February 1942 on the physics of the arc and the transfer of metal in arc welding. After discussing historical developments and experiments with arcs, the theory of electrical discharges in gases is dealt with. In special sections the forces acting on the electrodes and on the transfer of metal, alternating-current arcs, probe measurements, arcs in artificial atmospheres and the magnetic blow are considered. The bibliography contains 178 references.

The Fabrication and Testing of Fusion Welded Pressure Vessels. S. H. Griffiths. (Engineering Inspection, 1943, vol. 8, Spring Issue, pp. 4-23). The author describes the equipment and technique, including X-ray inspection, employed to produce welds of high quality in pressure vessels at the works of John Thompson (Wolverhampton), Ltd. The fully automatic Unionmelt welding machines are employed for many of the welds in thick plate. The Unionmelt process has been described previously (see Journ. I. and S.I., 1939, No. I., p. 284 A).

Structure of Butt-Welded Steel Tubing. H. J. Mastenbrook and H. J. Steffen. (Welding Journal, 1943, vol. 22, Jan., pp. 52-S-56-S). The author reports on an investigation of the structure and hardness of oxy-acetylene butt welds in chromium-molybdenum steel tubes $1\frac{3}{4}$ in. in outside dia. and 0.084 in. thick. The heat-affected area could be divided into three zones, the first extending for about $\frac{5}{8}$ in. from the centre of the weld. This zone had cooled from above the upper critical point, and it had a coarse Widmanstätten structure near the centre, which became finer as the distance from the centre increased. The second zone extended $\frac{5}{16}$ in. beyond the first; this had cooled from a temperature between the upper and lower critical points, and was composed of a mixture of Widmanstätten and recrystallised structures. The third zone extended for a $\frac{1}{4}$ in. beyond the second and had cooled from below the lower critical point; the structure changed from recrystallised grains near the inner edge to that of the parent metal at the edge farthest from the weld.

The Arc Welding of High-Tensile Alloy Steels. E. C. Rollason. (Metal Treatment, 1943, vol. 10, Spring Issue, pp. 3-14). The author discusses the problems and defects which arise in the welding of high-tensile alloy steels. He describes in detail the necessary equipment and welding technique, pointing out that a full knowledge of the metallurgical characteristics of the steel in question is essential to the development of a suitable procedure.

Working Out Techniques for Welding Armor Plate. E. G. Biederman. (Iron Age, 1943, vol. 151, Jan. 21, pp. 46-50). The

author describes a series of tests on butt-welded joints in alloy steel armour plate. From these it was established that the best welding technique was to prepare the edges in the double-V form with equal included angles of at least 45° and to use a copper backing strip at the root when depositing the first bead.

Metallic Arc Welding of High Sulphur Free-Cutting Steels. T. Swinden and H. F. Tremlett. (Transactions of the Institute of Welding, 1943, vol. 6, Jan., pp. 1-8). Practical difficulties encountered in the arc welding of low-carbon high-sulphur steels led to the investigations described. These covered weldability and mechanical tests on steels of this type using mild steel and dead soft steel electrodes. Similar tests were carried out on leaded low-carbon high-sulphur steel using dead soft electrodes only. The results showed that, while certain variations in weldability occurred with both types of electrodes, the dead soft type exhibited, in general, definite superiority over the mild-steel type. Good results were also obtained by welding leaded low-carbon high-sulphur steel with dead soft electrodes.

The Production of Single Spot Welds in Mild-Steel Plates of $\frac{1}{8}$ ", $\frac{1}{4}$ " and $\frac{3}{8}$ " Thickness. J. Dearden and H. O'Neill. (Transactions of the Institute of Welding, 1943, vol. 6, Jan., pp. 8-23). The authors report on an investigation to determine the optimum conditions for making a single spot weld in $\frac{1}{8}$ -in., $\frac{1}{4}$ -in. and $\frac{3}{8}$ -in. mild-steel plates. The effects of current, timing, welding and upset pressure, electrode tip diameter, heat control and interrupted current were assessed. The conclusions were: (1) A good-quality single-spot weld of high potential breaking load is liable to premature test failure by tearing, owing to bending of the component plates during testing; the breaking loads are liable to be influenced by the dimensions of the test-piece. (2) Subject to (1), the breaking load of a spot weld is proportional to its size, and this is limited by the diameter of the electrode tips; for strong welds having shallow indentations large tips are desirable. (3) The elongation values obtained depend on the load and are independent of the mode of failure; as normalising reduces the breaking load and the extension *pro rata*, it does not improve the ductility of a spot weld in mild steel. (4) The resistance to impact of a spot weld depends almost entirely on the development of a fusion zone of adequate size within the weld. (5) Porosity does not appear to have any influence on the breaking load, which is largely determined by weld size. (6) Ejection of liquid metal between the plates must be prevented if deep indentation is to be avoided. (7) Welding pressure appears to have very little influence on the quality of spot welds, provided the current density is below 150,000 amp. per sq. in. (8) The application of upset pressure when welding $\frac{1}{4}$ -in. and $\frac{3}{8}$ -in. plates does not produce any combination of breaking load and indentation which cannot be obtained without upset pressure. (9) Current is the most important factor in determining weld

strength, current density being of secondary consideration. (10) Tip diameter is not critical, and a considerable increase in diameter can be tolerated in service, provided the current density is above a certain critical value for each diameter. (11) Interrupted current welding requires higher currents and greater energy consumption per weld without improvement in the properties of the weld. (12) Variation in the time for which the electrodes maintain mechanical pressure on the weld after shutting off the current (called "dwell time") has no appreciable effect on the breaking load.

A Consideration of Tests to Determine the Weldability of Steels for Arc Welding. J. G. Ball. (Transactions of the Institute of Welding, 1943, vol. 6, Jan., pp. 24-46). The author presents a comprehensive review and an analysis of weldability tests which have been evolved to measure the cracking tendency both of parent metal and weld metal, or to forecast the manner in which a welded joint would behave in a fabricated structure.

Reclaiming Tools. H. E. Fleming. (Steel, 1942, vol. 111, Dec. 7, pp. 122-124, 157, 158; Dec. 14, pp. 88-90). The author gives details of the low-temperature brazing techniques which have been successfully developed at the tractor plant of the International Harvester Co., Chicago, for repairing broken or worn high-speed steel tools.

Principles of Shrinking and Straightening Distorted Low Carbon Steel Used in Shipbuilding. M. D. Offen. (Welding Journal, 1943, vol. 22, Jan., pp. 14-16). The author describes the use of "strongbacks" and other mechanical pulling devices which, combined with the local application of heat and cooling media, will straighten plates which have been distorted by welding.

CLEANING AND PICKLING OF METALS

The "Fraser-Heller" Metal Degreasing System. (Engineering, 1943, vol. 155, Feb. 19, pp. 146-147). The cleaning of metal parts by trichlorethylene vapour degreasing is, in effect, liquid degreasing, since the vapour condenses and is deposited in liquid form on the metal parts, its quantity being limited by their thermal capacity; inadequate degreasing therefore results not infrequently with thin sheet-metal parts, and where "dried-on" oil or soluble oil is involved. In the Fraser-Heller system, the plant for which is described in this article, the metal objects are first degreased with trichlorethylene vapour, and subsequently with a concentrated rain of the condensed solvent, and this condensate is treated so that it contains no grease picked up from previous operations.

Blast Cleaning Equipment—Its Care and Maintenance. D. C. Turnbull. (Iron Age, 1942, vol. 150, Dec. 31, pp. 36-39). The author makes recommendations on the maintenance of shot-blast

and centrifugal cleaning equipment. The adjustment of nozzles, hoses and air lines, the elimination of moisture from compressed air and the separation of dirt from used abrasives are dealt with.

Cleaning 20 and 155 mm. Shells. S. G. Hawley. (*Iron Age*, 1943, vol. 151, Jan. 21, pp. 42-45). The author describes the mechanised cleaning equipment for 20 mm. and 155 mm. shells at the works of Willys-Overland Motors Incorporated. Two proprietary brands of solution are used, one for cleaning and one for rust prevention.

The Development of Lathes for Ingots. H. Rübmann. (*Stahl und Eisen*, 1943, vol. 63, Mar. 4, pp. 177-179). The author describes the development of special lathes for trimming ingots to remove the inclusions which lie just under the surface. The tool-rests have two motions, one to follow the contour of the ingot, and the other to keep the tools at a constant angle to the surface it is cutting.

Constructional Methods and Materials for Pickling Tanks. A. J. T. Eyles. (*Mechanical World*, 1943, vol. 113, Mar. 5, pp. 247-248). The author describes and discusses the construction of wooden pickling tanks with special reference to methods of protecting the tie-rods and other metal fittings from corrosion.

I.R. Drop Compensation on Cleaning Lines. J. R. Erbe. (*Iron and Steel Engineer*, 1942, vol. 19, Dec., pp. 53-55). The author outlines the problem of controlling the speeds of the motors driving the uncoiler, scrubber rolls, drier rolls, pinch rolls, bridle rolls and coiler of a high-speed continuous cleaning line for steel strip, and describes the electrical equipment with which the speeds of the motors are synchronised.

COATING OF METALS

How to Choose Electroplating Equipment. A Bregman. (*Iron Age*, 1942, vol. 150, Dec. 17, pp. 50-55; Dec. 24, pp. 40-44). The author describes and illustrates many types of equipment and accessories for the electroplating of small parts, in particular horizontal-barrel plating containers, dipping baskets, conveyors, driers and polishing machines.

The Employment of Electro-Chemical Deposition in the Manufacture and Maintenance of Automobiles. R. E. Wilson. (*Proceedings of the Institution of Automobile Engineers*, 1941-42, vol. 36, pp. 211-233). The author discusses examples of the electro-deposition of metals, in particular nickel and chromium, in the automobile industry. On the possibility of hydrogen embrittlement, the author considers there is little danger of this provided the work is carried out under proper control, with moderate temperatures during pickling and etching, with inhibitors in the

solutions, and high current density combined with moderate temperatures, and that the parts are not hardened to an unnecessary degree, or are in themselves too highly stressed. Some stripping tests on rings of nickel deposited on 1-in. dia. steel shafts revealed that failure occurred by shearing of the steel just inside the nickel coating, and not by failure of the adhesion between the coating and the steel. In the machining of heavy deposits of nickel the first cut should be commenced near the centre of the part and traversed outwards until the surplus metal has been removed; this cuts away any globules of excess metal at the edge of the deposit without the tool digging into the base metal. In the plating of a shaft bearing surface with flanges, the deposit tends to build up at the edges of the flanges and on the centre of the shaft. When depositing chromium on shafts which are heavily shielded, the part should be prepared by reducing the diameter of the shaft on an area remote from the radii to less than the finishing diameter; the chromium is then deposited and to achieve the necessary thickness at the boundaries of the reduced area there will be an excess thickness at the centre which must be ground off afterwards.

Heat-Treated Duplex Electroplated Coatings. E. E. Halls. (Metal Treatment, 1943, vol. 10, Spring Issue, pp. 39-45, 60). The author describes the "Corronising" process which consists of applying thin composite coatings of nickel and zinc, or nickel and tin, by electrolysis and then subjecting the coated steel to a special heat treatment. The results of experience in England are compared with results reported earlier by R. Rimbach in the United States (see Journ. I. and S.I., 1942, No. I., p. 102 A).

Tool Life Increased by Improved Chromium Plating Process. T. E. Lloyd. (Iron Age, 1942, vol. 150, Dec. 10, pp. 43-49). The author describes a method which has been successfully used in the United States for increasing the life of high-speed steel tools. Chromium plating has not been satisfactory because the tool absorbed hydrogen in the plating bath and often became brittle at the face. In the improved method which prevents this embrittlement the plating solution is made up of 50 oz. of 99.75% chromium trioxide dissolved in water, to which 0.5 oz. of concentrated sulphuric acid is added. Allowance must be made for the sulphate content of the chromium trioxide when adding sulphuric acid to the bath. The bath temperature is kept between 110° and 150° F. and the current density is in the 130-200 amp. per sq. ft. range according to the size of the material being plated. The tool is placed with the cutting edge $\frac{1}{4}$ in. below the surface of the solution and it is made the anode for a short time with a high current density. The current is then reversed so that the tool becomes the cathode; lead or stainless steel anodes are used. After plating, the tool is rinsed thoroughly in cold water and dried; it is then transferred to an oil bath, held at 350° F., in which it remains for 1 hr., after which it is allowed to cool in air. It is the treatment in oil which

eliminates the hydrogen embrittlement. The results of machining tests on a large number of tools are given.

Hard Chrome Plating for Wear Resistance and Salvage. S. H. Brams. (Iron Age, 1943, vol. 151, Feb. 4, pp. 56-57, 112). Some examples are given of the increased life obtained by the hard chromium plating of dies and gauges.

Hard Chromium Plating. A. Fletcher. (Metal Finishing, 1942, vol. 40, Oct., p. 536). The author makes recommendations on the construction of racks for hard-chromium-plating equipment.

Clad Steel "Sandwiches" Welded by the Carbon Arc. T. S. Fitch and L. W. Townsend. (Iron Age, 1943, vol. 151, Feb. 18, pp. 54-59). The authors describe in detail the application of the carbon-arc welding process to the manufacture of steel sheet clad with stainless steel by the Jessop method. (See abstract entitled "New Cladding Method," Journ. I. and S.I., 1942, No. II., p. 113 A).

Metallic Coating to Prevent Corrosion. (Brown-Boveri Review: Iron and Coal Trades Review, 1943, vol. 146, Mar. 12, pp. 391-392). A description is given of the equipment for hot-dip galvanising. Careful temperature control of the bath is necessary to ensure long life, for the solubility of iron in zinc at 500° C. is 3.2 times, and at 550° C. 12.5 times, greater than it is at 460° C. Electrically heated baths are now designed so that the whole surface is fully utilised for the heat transmission at minimum temperatures. A tank to hold about 27 tons of molten zinc requires a power input of 180 kW.

Hot-Dip Galvanising Technique. Part VII. The Formation of Dross. Part VIII. The Heating of the Kettle and Its Temperature Control. G. Robinson. (Wire Industry, 1943, vol. 10, Feb., pp. 67-68; Mar., pp. 111-114). Continuation of a series of articles (see Journ. I. and S.I., 1943, No. I., p. 170 A). The conditions governing the formation of dross in a galvanising kettle for wire are discussed in Part VII. The one factor which has by far the most important effect on the iron-zinc alloy dross crystals is the temperature. The higher the temperature the more active is the zinc; there is a critical temperature at about 482° C. above which the reaction between the two metals becomes excessive. The higher the temperature, the larger will be the crystals. Careful temperature control is essential to avoid excessive dross formation. As materials for constructing the bath so as to resist the attack of molten zinc, steel lined with a boro-silicate or steel impregnated with aluminium have been suggested, but the author prefers a good quality mild steel low in manganese, silicon, sulphur and phosphorus. In Part VIII. the different results obtained by bottom heating and side heating galvanising kettles are explained by diagrams showing the movement of the molten zinc; side heating has definite advantages. A brief description is given of a mercury-in-steel thermocouple and temperature recorder suitable for zinc kettles.

High Frequency Heating Conserves Critical Tin. G. E. Stoltz. (Blast Furnace and Steel Plant, 1942, vol. 30, Dec., pp. 1357-1358). The author gives a brief outline of a process by which high-frequency current is applied to the tin coating on steel strip to melt it and produce a thinner and more uniformly distributed coating. Coils of strip can be electrolytically tinned at speeds up to 500 ft. per min. and inductor heating coils, rectangular in shape, have been designed with which the temperature of the strip can be brought up to 450° F. within 0.7 sec. after the strip enters the coil. The strip passes from the inductor coil through a water quenching tank. At one plant 60-cycle A.C. is rectified to D.C. and fed to vacuum-tube oscillators which convert it to 200,000 cycles per sec. at which it is fed to the inductor coil. The corrosion resistance of the tinplate is improved because the tin is melted and caused to flow so as to fill up any porous places.

Palm Oil—Its Utilization in the Steel Industry. R. P. Dunmire. (Iron and Steel Engineer, 1943, vol. 20, Jan., pp. 55-64). The author gives a comprehensive account of the properties of palm oil, how it is used in cold-rolling and tin-plating, how it deteriorates in service and the equipment and processes for cleaning and refining it after use in a tinplate mill.

Steel Clad with Gilding Metal. T. C. Campbell. (Iron Age, 1943, vol. 151, Jan. 14, pp. 33-34). The author gives a brief description of the process, developed by the Superior Steel Corporation, of cladding carbon steel strip with a layer of an alloy of 90% of copper with 10% of zinc. The finished material is now extensively used as a substitute for brass in manufacturing small arms cartridge cases.

Improving Deep-Drawing Qualities by Phosphatising. (Iron and Steel, 1943, vol. 16, Mar., pp. 255-256). Some data are presented which prove that phosphatising steel sheet reduces the power required for deep-drawing operations; it also enables an emulsion to be used as a lubricant instead of oil, decreases die wear and increases the number of operations which can be performed on the sheet without intermediate annealing. A phosphatised surface is capable of retaining twice as much oil as a bright uncoated surface. The oil is held mainly by the rough surface and is not stored up in the capillaries of the phosphatised layer.

Coating Nylon, Formvar etc. on Wire. (Wire and Wire Products, 1942, vol. 17, Dec., pp. 716, 730). A brief description is given of the dies and die holders developed by the E. I. du Pont de Nemours Company for coating wire for magnets with high-viscosity synthetic materials such as Nylon and Formvar. The dies are held between hairpin-like wires which permit them to swing freely in a plane at right angles to the axis of the wire.

Railroads Extend Use of Metallizing. (Machinist, 1943, vol. 86, Mar. 13, pp. 1354-1356). The equipment and technique for repairing worn piston rods, shafts and crankshafts in railway repair

shops by spraying molten metal is described and illustrated. Details are given of an automatic reversing device to attach to a lathe bed which reverses the movement of the spraying pistol when it gets to the end of the shaft.

Preparation of Hardened Surfaces for Metallizing. W. C. Reid. (Iron Age, 1943, vol. 151, Feb. 18, pp. 62-65). The author describes a simple method of roughening the surface of very hard steel so as to prepare it for metal spraying. A row of six electrodes of a high-nickel alloy is clamped between cooling discs in a holder and these and the steel to be treated are connected by flexible leads to the secondary coil of a small transformer with an open circuit voltage of 9 V. max. The surface to be sprayed is stroked lightly and rapidly with the ends of the electrodes; the heat generated at the points of contact causes a "metal foam" to be fused on to the base metal. This rough surface makes a very good bond for subsequent metal spraying. The method is called the "Fuse-Bond" process.

Reclaiming Worn Machine Parts by Metal Spraying. A. J. T. Eyles. (Mechanical World, 1943, vol. 113, Feb. 5, pp. 133-136). The author describes and illustrates the process of metal spraying, giving details of the preparation of the surface before spraying and the finishing by turning, grinding and polishing.

The Reclamation of Worn Parts by Metal Spraying. W. E. Ballard. (Proceedings of the Institution of Automobile Engineers, 1941-42, vol. 36, pp. 77-94). The author discusses the advantages and limitations of metal spraying, in particular as a means of repairing worn automobile parts. It is common practice to cut a screwthread on the surface to be sprayed to give good adhesion, and long experience has shown that this does not decrease the fatigue strength of highly stressed sprayed parts. A metal-sprayed surface contains minute pores which hold lubricating oil very tenaciously, and, in prolonged tests on various types of automobile engine bearings, much less wear and a lower seizing tendency has been noted with these surfaces than with very smooth hardened surfaces. Several examples of the advantageous use of metal spraying in war-time are described.

Mechanics of Enamel Adherence : XIV., (1) Rôle of Cobalt Oxide in Metal and Oxide Precipitation during Ground-Coat Firing Cycle and (2) Determination of Temperature and Time Intervals of Precipitation. R. M. King. (Journal of the American Ceramic Society, 1943, vol. 26, Feb., pp. 41-48). Continuation of a series of articles (*see* Journ. I. and S.I., 1937, No. I., p. 233 A). The rôle of cobalt oxide in metal precipitation is explained on the basis of the influence of cobalt oxide on the reaction $4\text{FeO} \rightleftharpoons \text{Fe} + \text{Fe}_3\text{O}_4$. The temperature intervals during the firing cycle at which precipitation takes place and the relative rates of precipitation in ground coats of varying composition have been determined by a method of electrical conductivity at high temperatures.

Some of the Important Possibilities of Infra-Red Lamp Heating, including the Drying of Lacquer in Food Cans. F. E. Rowland. (Association of Supervising Electrical Engineers: Sheet Metal Industries, 1943, vol. 17, Jan., pp. 77-80). The author describes some infra-red lamp installations and the advantages of using them for drying paint and lacquer.

PROPERTIES AND TESTS

Metal Properties. (Heat Treating and Forging, 1942, vol. 28, May, pp. 228-229, 237; June, pp. 276-277, 286, 289; July, pp. 333-334). The terms used in the mechanical testing of steel are simply explained.

The Mechanical Testing of Materials with Special Reference to the Testing of Welds. V. E. Green. (Engineering Inspection, 1943, vol. 8, Spring Issue, pp. 24-28, 32). The author describes several forms of mechanical test for metals and the particular purpose of each. Descriptions are given of the Avery-Schenck revolving cantilever-beam testing machine and the Avery-Schenck pulsator fatigue-testing machine.

Repeated Stress Relieving Treatments on Steel Plate. F. Eberle and T. Brick. (Metals and Alloys, 1942, vol. 16, Nov., pp. 894-901). The authors report the results of tensile, impact and creep tests on high-tensile steel plate 1 in. and 4 in. in thickness, on carbon-molybdenum steel plate and on manganese-vanadium steel plate, the object being to determine whether repeated stress-relieving heat treatments lowered the mechanical properties of the plate. The tensile and impact strengths at room temperature were not appreciably affected by up to ten repeated treatments, and the creep strength was unaffected by five treatments.

The Magnetic Powder Method of Inspecting Weldments and Castings for Subsurface Defects. C. H. Hastings. (Welding Journal, 1943, vol. 22, Jan., pp. 43-S-51-S). The author describes an investigation at the Watertown Arsenal of factors influencing the detectability of defects in steel plate using the magnetic powder method. Low-alloy structural steel plates of different thicknesses were used and the edges were specially machined to make a tight-fitting tongued and grooved joint; defects of different width, height and distance from the surface were produced by varying the length, thickness and position of the tongue, the gap between the end of the tongue and the bottom of the groove constituting the defect. The joint was welded along the top and bottom surfaces to form a continuous magnetic path and any accidental defects in welding were not in line with the purposely created gap along the tongue. Two welding generators in parallel were used for the magnetising current which could be varied in the 200-2000 amp.

range. The test data are presented in numerous tables and graphs. The general conclusions were: (1) Many types of defects can be detected by the magnetic powder process and they are easiest to detect when one dimension is appreciably larger than the others; (2) the orientation of a defect with respect to the surface on which the electrodes are placed influences the detectability; (3) rounded defects are difficult and sometimes impossible to detect; (4) the depth of the defect from the surface is the most important factor affecting the detectability; (5) defects can be detected at greater depths in thick plate than in thin plate; (6) the width of the powder pattern increases with the width and depth of the defect; (7) as the depth of the defect from the surface increases, the pattern becomes less sharply defined; (8) the pattern intensity increases with the magnetising current and the height of the crack; (9) the surfaces of the part may be injured by overheating or sparking at the electrode contacts and this can be prevented by using lead pads; (10) the dry magnetic powder should be dusted into still air between the electrodes without allowing the container to touch the surface to be tested; and (11) much can be learnt by watching the formation of the pattern.

Fluorescent Magnetic Inspection. W. E. Thomas. (Metals and Alloys, 1942, vol. 16, Nov., pp. 886-890). The author compares the advantages and limitations of the Magnaflux and Magnaglo methods of detecting very fine cracks in steel. The latter method appears to be the same as that known in England as Glo-Crack (see Journ. I. and S.I., 1942, No. II., p. 217 A).

Statistical Investigations on the Causes of Fracture in Tyres and Rails. A. Pusch. (Iron and Steel Institute, 1943, Translation Series, No. 135). An English translation is presented of a paper which was published in Stahl und Eisen, 1942, vol. 62, Dec. 3, pp. 1022-1053. See Journ. I. and S.I., 1943, No. I., p. 137 A.

End-Quench Hardenability Curves of NE Steels. (Metal Progress, 1942, vol. 42, Nov., p. 857). Eight groups of hardenability curves are presented showing the changes in hardness at increasing distances from the quenched end of specimens of S.A.E. steels and of similar National Emergency steels of the same grain size.

Cast Iron as Bearing Material. P. Grodzinski. (Machinist, 1942, vol. 86, Dec. 19, pp. 228E-229E; Dec. 26, pp. 234E-235E). In the first part of this series the author discusses the properties of cast-iron bearings summarising data supplied by a number of manufacturers. He presents: (a) Curves from which the maximum permissible running speeds to produce a given temperature increase can be calculated given the bearing diameter and the specific running speed; (b) the results of tests in which the seizure pressure of cast-iron bearings under given running conditions were compared with those of bronze bearings.

The Specific Heat of Pure Iron at Low Temperatures. K. K. Kelley. (Journal of Chemical Physics, 1943, vol. 11, Jan., pp. 16-

18). Specific heat measurements of iron of 99.94% purity were determined throughout the temperature range of 52°–298° K. These measurements were undertaken because five of the sets of determinations previously recorded in the literature are in disagreement. The results of the present work are thought to be accurate within 0.3% and they confirm the work of A. Eucken and H. Werth and of F. Simon and B. C. Swain rather than the determinations by W. H. Rodebush and J. C. Michalek and by E. H. Griffiths and E. Griffiths.

Boron Steels Increasingly Favoured. N. F. Tisdale. (Iron Age, 1943, vol. 151, Feb. 4, pp. 41–44). The author discusses in what form boron can be added to iron and steel and its effect on the properties. A ferro-boron has been developed containing carbon 1.5%, boron 11% and silicon 3%; this has a low melting point and readily dissolves in molten cast iron and steel; the recovery of boron is 85–90%. In melting down cast iron scrap containing boron about 50% is recovered. In high-silicon cast irons up to 0.19% of boron can be added to obtain a finer grain and increased hardness. Steel containing as little as 0.007% of boron has exhibited hot-shortness; the optimum amount to add appears to be 0.0025–0.0030%; in this range a greater depth of hardenability is obtained. The addition of boron to steel coarsens the grain slightly, but this can be counteracted by a very small increase in the amount of aluminium. Steel containing from 0.20% to 0.60% of carbon is most responsive to boron additions. Adding boron to steels with less carbon than this may produce too high a core strength after case-hardening and it may then be necessary to reduce the manganese content; for such steels boron additions of only 0.001–0.002% are sufficient. With alloy steels it has been found that adding 0.003% of boron is equivalent in its effect to 0.01% of nickel, 0.30% of chromium, 0.10% of molybdenum, 0.12% of vanadium or 0.20% of manganese.

The Effect of Silicon on Hardenability. W. Crafts and J. L. Lamont. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1542: Metals Technology, 1943, vol. 10, Jan.). The authors report the results of a laboratory investigation of the effect of silicon on the hardenability of steel. Factors were determined for a number of steels which enabled the effects of silicon, manganese and aluminium on the hardenability of steel to be calculated; these were applicable within the ranges of 0.20–0.55% of carbon, 0.50–1.75% of manganese, 0.20–2.00% of silicon and up to 0.40% of aluminium. The multiplying factor for silicon increases directly in proportion to the silicon content up to at least 2% of this element. The steels tested in this investigation confirmed the validity of M. A. Grossmann's method of calculating hardenability (*see* Journ. I. and S.I., 1942, No. II., p. 219 A).

Notes on the Influence of Sulphur and Phosphorus on the Properties of Steel. E. Gregory. (Metal Treatment, 1943, vol. 10,

Spring Issue, pp. 15-22). The author discusses how sulphur and phosphorus affect the properties of steel pointing out why it is not always necessary to insist on very low contents of these elements. The theory that the manganese content should be at least 6-7 times the sulphur content in order to counteract completely the detrimental influence of sulphur in the hot-working properties of steel is not borne out in practice. The fact that sulphur can function as a powerful deoxidant of molten steel has not been fully appreciated in the past, and its influence on the cracking of ingots of normal manganese contents must be dissociated from the disintegration of steel when insufficient manganese is present to convert the whole of the sulphur into relatively harmless sulphides. For certain specific purposes high-sulphur grain-controlled steels can be substituted for some of the more orthodox low-alloy case-hardening steels hitherto used. The production of very low phosphorus steels may be accompanied by over-oxidation; this is of paramount importance in connection with fully killed carbon and alloy steels. Phosphorus contents of the order of 0.015% may be accompanied by difficulties in forging and rolling, largely due to the presence of surface seams. Residual phosphorus contents between, say, 0.025% and 0.050% have little or no influence on the final mechanical properties of many structural steels made by the basic open-hearth process, provided that they are free from segregation.

Tool Steels for Working Hot Metals. H. Treppschuh. (Stahl und Eisen, 1943, vol. 63, Mar. 11, pp. 189-199). The author reviews the development and properties of special steels for making forged and rolled tools for working hot metals. The tools and machines dealt with include large and small forging hammers and presses, upsetters, mandrels, rams, dies for many purposes including pressure die casting, hot shears, hot saws and punches. Information is given on the chemical composition, heat-treatment, hardness retention, hot-strength and applications of the various steels.

Heat Resisting Alloy Steels. C. K. Lockwood. (American Society for Metals: Canadian Metals and Metallurgical Industries, 1943, vol. 6, Feb., pp. 14-19). The author reviews the properties of heat-resisting alloy steels, classifying them in the following groups: (1) 4-6% chromium steels; (2) 12-14% chromium steels; (3) 16-18% chromium steels; (4) 25-30% chromium steels; (5) 18/8 chromium-nickel steels; (6) 25/12 chromium-nickel steels; and (7) 35/15 nickel-chromium steels. In working out a relationship between the various elements in the steels belonging to group (6) it is necessary to consider the chromium content minus sixteen times the carbon content, because carbon combines with about sixteen times its weight of chromium to form Cr_4C . The ratio between the ferrite- and austenite-promoting elements is expressed by

$$\frac{\text{Cr} - 16\text{C}}{\text{Ni}}$$

and the numerical value of this ratio is called the "ratio factor" for the alloy. It can be shown by phase diagrams and microstructures that when this ratio is less than 1.7 the alloy will be austenitic; when it is above 1.7 it will be partially ferritic after heating in the critical range. Samples of this 25/12 alloy that are not magnetic as cast can be made magnetic by heating them to about 2000° F. and quenching them in water if there is any tendency for the ferritic phase to be present.

A Metallurgical Study of German and Italian Aircraft Engine and Airframe Parts. Section XII. Miscellaneous Engine Parts. Section XIII. Airframe Components. Section XIV. Miscellaneous Parts. (Metallurgia, 1943, vol. 27, Jan., pp. 98-105; Feb., pp. 123-134; Mar., pp. 181-184). These constitute the concluding parts on the report by the Aero-Components Sub-Committee of the Technical Advisory Committee on Steels, Ministry of Aircraft Production. (See Journ. I. and S.I., 1943, No. I., p. 141 A).

The Functions and Organisation of the Chemical and Metallurgical Laboratory in the Light Engineering Industry. H. Silman. (Sheet Metal Industries, 1943, vol. 17, Feb., pp. 279-284, 290; Mar., pp. 461-466, 496). The author discusses the organisation, limitations and scope of chemical and mechanical testing laboratories with a view to assisting those industrial concerns which are faced, owing to war conditions, with the problem of instituting a laboratory for the first time.

METALLOGRAPHY AND CONSTITUTION

Sir William Chandler Roberts-Austen, K.C.B., D.C.L., D.Sc., A.R.S.M., F.R.S. S. W. Smith. (Institution of Mechanical Engineers, The Iron and Steel Institute and The Institute of Metals: Metallurgia, 1943, vol. 27, Mar., pp. 169-177). This is the text of a lecture on the life and work of the late Sir W. C. Roberts-Austen, delivered on the centenary of his birth, on March 3, 1843.

New Method of Etching on Metals. (Engineer, 1943, vol. 175, Mar. 12, p. 217). Particulars are given of a simple and rapid method of etching trade marks, part numbers, patent numbers, &c., on the surface of metals such as high-speed steel, stainless steel and stellite. The process is electrolytic and makes use of a standard waxed stencil on which are typed or printed the required words or designs. This is placed between the metal article, which forms the anode, and an absorbent pad containing the etching fluid, which is connected to the cathode of a 15-V., D.C. circuit.

FUEL

(Continued from pp. 3 A-5 A)

Analyzing Heat Flow in Cyclic Furnace Operation. C. B. Bradley and C. E. Ernst. (Mechanical Engineering, 1943, vol. 65, Feb., pp. 125-129). The authors discuss the determination of heat flow under unsteady conditions and compare the results obtained in a particular heat-flow problem by the direct-test method and by an electrical heat-and-mass-flow analyser developed by V. Paschkis and H. D. Baker (*see* Journ. I. and S.I., 1942, No. I., p. 133 A). It is shown that the analyser can be used to determine the average heat flow through a great variety of wall thicknesses and constructions in order to establish which is the most economical thickness and combination for a particular purpose.

The Calculation and Design of Induction Burners. W. Heiligenstaedt. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 529-538). The advantages of induction gas burners include the fact that with them the supply of heat is easily controlled by a single valve and that the correct proportioning of the gas and air is automatic. In this paper the author discusses the design and operation of these burners, the results achieved with them and the effect of changes in the furnace pressure. The lower limit of furnace load is governed by the velocity of the gas-air mixture at which the mixture back-fires in the burner, and this velocity, which is found experimentally, is of great importance in burner design. Having regard to these facts, methods of calculating gas velocities, gas pressures and burner dimensions for mixtures of coke-oven gas and air are explained with examples.

Combustion Hazards. T. A. Cohen. (Steel, 1943, vol. 112, Jan. 18, pp. 60-64). The author describes some safety devices for use in industrial furnaces fired with oil, gas or pulverised coal. These consist of (a) fans for purging a furnace of explosive gas mixtures before lighting; (b) electrical controllers for fuel valves which are based on the electrical resistance of a flame; and (c) fuel-valve controllers actuated by a photo-electric cell in such a way that failure of the flame causes the fuel supply to be instantly cut off.

Washery at Temple Pit of the Waterloo Main Colliery Co., Ltd. (Iron and Coal Trades Review, 1943, vol. 146, May 21, pp. 751-754). An illustrated description is given of the coal-washing plant at the Temple Pit of the Waterloo Main Colliery Co., Ltd. This washery works on a modified Rhéolaveur system and is designed to treat 100 tons of raw coal (up to 4½-in. size) per hr.

Effect of Oxidation on Reactivity and Swelling of Illinois Coals. O. W. Rees and W. F. Wagner. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Mar., pp. 346-348). The authors report on tests designed to study the characteristics of

Illinois coals, in particular the effect of oxidation of the whole coal, as well as its constituent bands (vitrain, clarain, durain and fusain) on the ignition temperature as measured by a reactivity test and the British Standards Institution swelling test.

Coal Oxidation. W. Fuchs, T. S. Polansky and A. G. Sandhoff. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Mar. pp. 343-345). Properly oxidised bituminous coal is readily soluble in the organic solvent furfural, and the recovery of both solvent and solute offers no serious problem. The ash-free carbonaceous material thus obtainable has numerous applications in the production of heat, power and chemical commodities. In this paper the authors describe a three-stage method of oxidising the coal, using a greatly diminished amount of nitric oxide, to obtain a product which is easily soluble in cold furfural, as well as the preparation and properties of the solutions.

Some Physical Characteristics of By-Product Coke for Blast Furnaces. C. C. Russell and M. Perch. (American Institute of Mining and Metallurgical Engineers, 1943, Technical Publication No. 1520). The authors describe the A.S.T.M. and other methods adopted in the United States for obtaining data on the properties of coking coals and blast-furnace coke. Data on the characteristics of cokes and how these are affected by variations in coal quality and the coking process are presented.

PRODUCTION OF IRON

(Continued from pp. 5 A-10 A)

Kaiser's Plant Begins Initial Operation. (Pacific Factory : Steel, 1943, vol. 112, Jan. 18, pp. 76-78, 94). Some particulars are given of an iron and steel works which is in course of erection near Fontana in Southern California. The blast-furnace, producing 1200 tons of iron per day, has already been blown in. There are also a very large sintering plant, six 185-ton open-hearth furnaces, two batteries of 45 Koppers-Becker coke-ovens with by-product recovery plant and a rolling mill for plates and sections. This is the first plant of its kind to be built on the Pacific coast of the United States.

Increasing Blast-Furnace Efficiency with a Simultaneous Saving in Coke. E. Senfter. (Iron and Steel Institute, 1943, Translation Series, No. 139). This is an English translation of a paper which appeared in Stahl und Eisen, 1942, vol. 62, Dec. 10, pp. 1041-1052. (*See* Journ. I. and S.I., 1943, No. I., p. 120 A).

Blast Furnace Practice. C. W. Miller. (Australasian Engineer, 1942, vol. 42, Dec. 7, pp. 17-29; 1943, vol. 43, Jan. 7, pp. 19-26; Feb. 8, pp. 12-13, 45-46). The author discusses the salient features of modern blast-furnace practice with special reference to the

operations at the plant of Australian Iron and Steel, Ltd., Port Kembla. A brief historical introduction outlines out-standing developments in blast-furnace design and operation leading to present-day practice. Reference is made to the design, construction and operation of a modern blast-furnace and its auxiliary plant, including the assembly and treatment of raw materials and the handling and disposal of products. The location and functioning of blast-furnaces in relation to other sections of steelworks plant are discussed.

Merwinite in the System CaO-MgO-SiO_2 . T. W. Parker and R. W. Nurse. (Iron and Steel Institute, 1943, this Journal, Section I). Merwinite has been known for some time as both a natural and an artificial mineral, but has not been detected as a stable phase in the system CaO-MgO-SiO_2 . The present work establishes the primary phase field of merwinite in this system, and gives the position of the invariant points with the neighbouring fields of larnite, akermanite, monticellite and periclase. The pure mineral itself melts incongruently at 1590°C. , forming 2CaO.SiO_2 and liquid.

The application of the data to problems of dolomite-silica refractories is discussed. It is shown that compositions of this type should be completely stable to both falling and hydration under all conditions of heating and cooling, when the CaO/SiO_2 ratio is less than 1.20, but that such mixtures form relatively large percentages of melt at fairly low temperatures and would therefore probably not be satisfactory refractories.

It is well known that falling blast-furnace slags can be stabilised by substituting MgO for part of the CaO in the slag composition, and, in practice, it appeared that stabilisation by this means covered a wider composition range than could be predicted on existing phase data. It is shown that the interposition of a merwinite primary field leads to deductions giving a greater agreement between theory and practice.

The data also provide confirmation of one point in Bowen's studies on the metamorphosis of siliceous limestone.

Iron Powder. C. Hardy. (Metal Progress, 1943, vol. 43, Jan., pp. 62-64, 126). The author discusses the characteristics of five different kinds of iron powder and their use in powder metallurgy. These kinds are : (1) Powder made from bar ends and sheet cuttings of Swedish iron ; (2) carbonyl iron powder ; (3) powder from Swedish sponge iron ; (4) powder from the reduction of mill scale ; and (5) electrolytic iron.

FOUNDRY PRACTICE

(Continued from pp. 10 A-11 A)

Scientific Method in the Foundry Industry. B. S. Morgan. (Institute of British Foundrymen : Foundry Trade Journal, 1943, vol. 69, Apr. 22, pp. 323-326). The author stresses the need for the rationalisation of knowledge of foundry technique and makes recommendations on the reporting of test results and other data, statistical methods of investigation, and the need for reviews of the technical literature and group research.

Metal Melting Cost in a Gray Iron Foundry. A. E. Grover. (Foundry, 1943, vol. 71, Jan., pp. 73-74, 159-162). The author describes in detail a costing system based on entries on cost cards, examples of which are reproduced, which enables the melting cost in a grey iron foundry to be accurately computed.

Studies of Foundry Practice in the United States. E. O. Lissell. (Jernkontorets Annaler, 1943, vol. 127, No. 2, pp. 35-59). (In Swedish). The author reviews developments and methods in American iron and steel foundries from his own observations during a recent visit. Descriptions are given of a wide variety of foundry equipment including the Griffin hot-blast cupola; this incorporates a recuperator to heat the blast and automatic control of the CO/CO₂ ratio in the cupola gases.

The Rocking Electric Furnace—A Silver Anniversary. H. W. Gillett and A. E. Rhoads. (Electrochemical Society, Apr., 1943, Preprint No. 83-3). In the first part of this paper H. W. Gillett presents a brief outline of the first trials in the development of the rocking electric furnace in the period 1911 to 1918. In the second part A. E. Rhoads covers the development of the Detroit rocking furnace in the next twenty-five years. Over 800 of these furnaces are now in operation for non-ferrous metals and iron and steel castings. This furnace has proved to be very useful in the foundry for producing small steel heats between iron heats at convenient times during the day. Some of the automobile manufacturing companies use this furnace to produce up to 1-ton heats of special steels.

Briquetting is Found Important Aid in Salvaging Operations. A. W. Wood. (Steel, 1943, vol. 112, Feb. 8, pp. 84-86). The author briefly describes the plant used by the Westinghouse Electric and Manufacturing Co. for briquetting the large quantities of cast-iron borings and steel turnings produced in their machine shops. The installation consists of a crusher for reducing the size of the turnings, a blower system which carries the crushed material into an overhead hopper, a hydraulic briquetting machine with a ram working at 2300 lb. per sq. in., and a conveyor to remove the briquettes. The capacity is about 1000 2-lb. briquettes per hr.

These briquettes are used as raw material in the foundry and help to make up for the shortage of scrap metal.

The Effect of Copper Content and Low Temperature Pretreatment of Some White Irons on Malleabilization. A. Elsea and C. H. Lorig. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1032-1058). The authors report on an investigation of the effect of copper additions, of low-temperature preheating and of the first-stage holding temperature on the time required to malleabilise white cast iron. The conclusions reached were: (1) A white iron of the composition used in this study responds more rapidly to malleabilising treatment if (a) it is held at a higher temperature during first stage graphitisation, (b) it is heated more slowly to the holding temperature, (c) it contains copper, and (d) it is subjected to a preliminary treatment at about 600° F. for 8 hr. (2) The effects of copper in accelerating the first and second stages of graphitisation are sharply intensified by the preliminary treatment. (3) The combined effect of copper and preliminary treatment is to reduce drastically the size of the temper-carbon nodules. (4) The size of the nodules formed in white malleable iron containing 0.6-2.0% of copper after a low-temperature pretreatment is not affected by the holding temperature, or by the rate of heating to the first stage graphitising temperature. (5) Pretreatment increases the tendency for a rim of carbide particles to persist during first stage graphitisation, but has little effect on the pearlitic frame found at the completion of second stage graphitisation, provided all the massive carbide has previously been decomposed. (6) Copper is not effective in removing the rim of carbide particles found during first stage graphitisation, but has a marked effect in reducing the amount of pearlite in the frame sometimes found on completion of the second stage graphitisation.

Trench Mortar Bombs Pass Critical Inspection. P. Dwyer. (Foundry, 1943, vol. 71, Jan., pp. 66-69, 151, 152). The author describes the plant and processes at a Canadian foundry now manufacturing large quantities of steel trench mortar bombs 9½ in. long and 3 in. in dia.

Progress Report on Investigations of Effect of High Temperatures on Steel Sands. No. 3—Effect of Ramming. J. R. Young. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 977-993). The author reports the results of research work on steel moulding sands carried out at Cornell University since the publication of Progress Report No. 2 by the Sub-Committee on the Physical Properties of Steel Foundry Sands at Elevated Temperatures (see Journ. I. and S.I., 1943, No. I., p. 78 A). The tests recorded were made on two sand mixtures, one consisting of 90% of silica sand with 10% of fireclay and the other of 95% of silica sand with 5% of fireclay. Some of the conclusions reached from the tests were: (1) For green sand, the total ramming energy is a more reliable index of the degree of ramming than the apparent

density of the rammed sample; (2) for the mixtures tested, an increase in the ramming intensity appears to lower the peak of the hot-strength/temperature curve; and (3) the maximum hot strength is reached at higher temperatures with the mixture containing the lower proportion of fireclay.

Steel Foundry Sands. E. C. Pigott. (Foundry Trade Journal, 1943, vol. 70, May 27, pp. 71-73, 77). The author discusses the properties and preparation of moulding sands for steel castings. The influence of water is most marked in bonded sands; for green-sand casting generally, the most suitable proportion is from 2% to 4%. The dry strength of mixtures containing emulsified binder is much improved by a moisture content of 1.5%. Sulphite lye gives a higher dry strength than molasses or resin; it yields, however, only a moderate green strength, and the finished surface is not very resistant to abrasion. For mixtures of silica sand and clay, the sand grains should be fairly uniform in size, semi-angular or angular, either rough or having a thin film of bond. Leighton Buzzard sand permits a very permeable mixture which strips very well, but imparts a rather rough surface to the casting. Though Ryarsh sand leaves a very smooth surface, it is only sufficiently permeable for small thin castings.

British Resources of Steel Moulding Sands. W. Davies and W. J. Rees. (Iron and Steel Institute, 1943, this Journal, Section I). In the First Report of the Moulding Materials Sub-Committee (a committee appointed by the Steel Castings Research Committee of The Iron and Steel Institute and The British Iron and Steel Federation) attention was directed to certain crushed grits and it was considered desirable to make a more complete investigation of the grits and sandstones accessible to steelmaking districts to see whether they could be used in the preparation of moulding materials for steel foundries. The present paper embodies the results of this investigation; it is divided into five parts each dealing with a particular district. The whole report takes up 101 pages, and the first half of it consists of Part I on the Upper Carboniferous grits and sandstones of the Peak District, which is within easy reach of Sheffield, Lancashire and the Midlands. Attention is directed to the relationship between the petrology and the moulding characteristics of grits, and it is shown from a petrological examination that to determine the mineralogical composition (by micrometric analysis) and the microstructure, useful indications can be obtained of the form of the mechanical-grading curve, the green strength and permeability, and the refractoriness. The important petrological features of grits suitable for steel-moulding purposes are discussed first; these are: (a) The grain size should be uniform and between 0.3 and 1.0 mm. (b) Sintering in the quartzitic aggregates should be simple, so that the proportion of composite grains in the crushed material will be small. It also seems desirable that the quartz grains should be free from strain. (c) The quartz content should be

not less than 80%. (d) The content of sericite and kaolin should not be high, because of their effect in increasing sinterability; the presence of some limonite is advantageous, but its proportion should not be high. A felspar content as high as 10% may not be detrimental if it is fresh, although a high felspar content reduces the ultimate refractoriness of the crushed grit.

Certain of the crushed grits have characteristics similar to those of the synthetic moulding materials, based on high silica sands, at present used in steel foundries. In the first appendix to this part detailed petrological descriptions of thirty rock samples are given, and this is followed by a second appendix in which data on the chemical composition of the rocks are presented. Part 2 deals with the Lower Carboniferous sandstones of Rothbury Forest and Alnwick Moor in Northumberland. These sandstones occur within easy reach of the Tyneside foundries. Geologically, they can be referred to two groups, the Fell Sandstone Group and the Scremerston Coal Group. The sandstones of the former group are so friable that in many cases they can be crushed between the finger and thumb; the resultant sand contains 95% or more of quartz. By simple washing, the quartz content can be increased to more than 98%. Consequently the Fell Sandstones are of particular interest as a source of high-silica sand. The sandstones of the Scremerston Coal Group in this area are, in general, too fine-grained and compact to be of use for steel-moulding, though one of them may be of service. Part 3 is devoted to the moor grit of North-East Yorkshire; this grit occurs in two types, felspathic and quartzitic, and is within easy reach of the Tees-side works. Certain of the occurrences of the felspathic type are sufficiently coarse to be suitable for steel-foundries and details of their moulding properties are given. The texture of the quartzitic type varies from open to compact. The former can be crushed easily to yield a high-silica sand suitable for iron and steel foundries. The latter variety is of little interest. In Part 4 the Rotten-Rock moulding sands at Wolsingham in Durham are discussed. These friable sandstones are extensively worked to produce naturally bonded moulding sands for the steel foundries on the North-East Coast. Attention is directed to the mineral constitution of the bond; it is indicated that a hydrobiotite bond is preferable to a sericite bond. In Part 5, which deals with the Permian yellow sands of Durham and Yorkshire, it is shown that these have been exploited for iron-moulding but not for steel castings. It is possible that some of the more refractory occurrences described could be used in steel-moulding sands with the addition of bonding clay.

The Gating of Castings. E. W. Harding. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 69, Apr. 29, pp. 343-345). A statistical analysis of the causes of defective castings has shown that 30% to 50% of them can be classified under the heading of incorrect gating. The function of the gate is obviously

to introduce molten metal into the mould, but certain conditions must be fulfilled so as to provide: (1) Efficient sand and slag trapping; (2) correct heat distribution; (3) minimum mould surface erosion; and (4) a suitable rate of pouring. To trap sand, it may be either floated out or strained out. The systems mainly employed for slag-trapping are: (a) Cope runner bar with drag ingates; (b) cope projection gates; (c) flow-by gate; (d) syphon skim gate; (e) whirl gate; and (f) strainer core. A knowledge of gating implies the ability to reason out what will happen when the metal is introduced into the mould in a certain way. A useful picture can be obtained by drawing isotherms to represent the temperature gradients during solidification; by this means it is possible to avoid incorrect practice and see more clearly the most suitable points of entry. Poor pouring-basin design and condition is one of the principal causes of dirty castings; however simple and obvious may be the principles underlying basin construction, this matter still seems to be neglected in practice.

Heavy Moulding Boxes. J. Timbrell. (Foundry Trade Journal, 1943, vol. 70, May 6, pp. 11-12). The author describes the design of large moulding boxes giving drawings of some of the features which he recommends.

Fluid Pressure in Foundry Practice. E. Longden. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, May 20, pp. 45-50, 52; May 27, pp. 65-69). The author explains the laws of fluid pressure and illustrates with numerous examples how these affect the design of moulds, gates, pouring basins and risers for castings of various shapes. The late evacuation of gases from moulds and cores is a greater cause of unsoundness than has yet been acknowledged or recognised by the average foundryman. Foundrymen will be impressed with the improvement which can be made by applying the combination of ample head pressure and generous gas outlets in moulds and cores, especially in difficult castings with complicated coring and design. Reference is made to the utilisation of atmospheric pressure to assist the feeding of steel castings in the manner described by H. F. Taylor and E. A. Rominski (*see* Journ. I. and S.I., 1943, No. I., p. 77 A). The importance of having adequate tackle and of consolidating the mould to withstand the stresses imposed by the head of fluid metal is stressed. The construction of casting pits for making castings up to 30 tons is described with special reference to the moulding and coring for a planing-machine stand and a 20-ton hydraulic cylinder, and calculations are made of the lifting pressure which will be exerted in these two cases on the top of the mould. Details are given of a cradle for handling cores of unusual length.

Castings for War Equipment. G. L. White. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, Mar., pp. 16-19). The author describes the plant and processes at the foundry of the Ford Motor Co. of Canada, Ltd. Brackelsberg, Electromelt and Swindell

electric furnaces produce the three steels used in the foundry. A 6½-ton furnace produces the steel for casting crankshafts. The other two grades of steel are produced in 3-ton furnaces, half of which are employed for melting and half for holding. Centrifugal casting for certain automobile and army tank parts has been developed to a remarkable degree. Egg-cup-shaped castings for the front wheel drives of lorries are made in this way in permanent moulds with temporary cores and a 50% saving in the weight of risers as compared with the stationary sand mould method has been achieved. Other examples of the successful production of centrifugally cast steel parts include bogie spring bearings cast in clusters of 52, clusters of 68 brake expander housings and clusters of 192 bogie spring spacers.

Theory of Shrinkage in Gray Cast Iron. G. A. Timmons. (American Foundrymen's Association: Foundry, 1943, vol. 71, Jan., pp. 80-81, 165-169). In the concluding part of this paper (see Journ. I. and S.I., 1943, No. I., p. 201 A) the author gives an account of tests on the shrinkage of 4-in. cubes of gray cast iron. The volume of the voids was determined by accurately weighing the cube in air and in water and by determining the density of a 1-in. cube cut from one of the bottom corners of the larger cube where the metal was certain to be solid. Under the conditions of casting with the low-alloy iron used, increasing the phosphorus from 0.015% to 0.123% increased the void volume from 0.35 c.c. to 2.96 c.c. Increasing the manganese from 0.52% to 1% decreased the void volume, but a further increase to 1.32% caused a very slight increase in shrinkage. Variations in the carbon between 3.01% and 3.44%, in the silicon between 1.39% and 2.85%, and increasing the sulphur content had no material effect on the void volume. Raising the pouring temperature from 2400° F. to 2850° F. increased the void volume from 1.9 c.c. to 4.5 c.c.

Testing the Wall Thickness of Intricate Castings. B. M. Thornton. (Engineering, 1943, vol. 155, May 7, pp. 361-362). In the direct-current method of testing the thickness of a casting wall from one side only, current is passed through the wall from two contacts; the potential drop caused by the flow of current, which is a measure of the wall thickness, is indicated on a galvanometer connected to two closely adjacent contacts. In the present paper the author describes a method for testing the walls of small intricate castings where it is difficult to make four suitable contacts in confined spaces. In this method the galvanometer contacts are not close to the contacts for the supply of current. In the case of a petrol engine cylinder block the connections to the direct current battery are made at each end of the block and the potential measuring contacts are made at the positions it is desired to test. Potential readings are first taken on a casting known to be sound, the contacts being located by templates. These templates are used on all the duplicate castings it is desired to test and any difference in the readings from those at the same

position on the master casting indicates a difference in thickness or a flaw.

Radiography as an Aid to Foundry Technique. W. Gladwell. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, May 6, pp. 3-8; May 13, pp. 23-25). The author describes the application of X-rays and gamma rays for the detection and location of faults in castings in heavy metals, particularly copper.

PRODUCTION OF STEEL

(Continued from pp. 11 A-13 A)

Chemistry at 1600. J. Chipman. (Transactions of the American Society for Metals, 1942, vol. 30, Dec., pp. 817-854). The author studies the theory of the reactions taking place at very high temperatures in a steel bath. Examples are given to explain the law of mass action which expresses the equilibrium constant of a reaction in terms of the activities of the reacting substances. Experimental methods have been developed for investigating the activities of substances dissolved in molten steel and slag. It is found that when certain molecular formulæ are arbitrarily assigned to these substances the activities of the constituents conform to the simple solution laws. It is shown how the equilibrium constant of a reaction may be obtained from thermodynamic data including data relating to free energy and to heat and entropy changes. A table of these quantities, applicable at steelmaking temperatures, is appended.

Recovering Scrap from Slag Dumps. G. R. Reiss. (Steel, 1943, vol. 112, Feb. 8, pp. 94-96). The author gives brief particulars of a type of scrap recovery plant developed by E. H. Heckett which is at work on many large slag heaps adjoining steelworks in the United States. Skulls are broken up by dropping a ball on them. Smaller pieces are loaded into a separating machine equipped with a conveyor which takes the slag over a magnetised drum. Large pieces consisting of steel and slag are put in a tumbling barrel holding from 6 to 8 tons; this breaks the slag off the steel and the latter is lifted out with a powerful magnet.

The Solidification and Cooling of Steel Ingots—Notes on an Examination of Three Typical Ingots. E. F. Law and V. Harbord. (Iron and Steel Institute, 1943, this Journal, Section I). A detailed microscopical examination has been made of two ingots, Nos. 36 and 59, and a partial investigation of a third ingot, No. 65, previously studied by the Ingot Committee (see Fourth and Sixth Reports on the Heterogeneity of Steel Ingots, *Iron and Steel Institute, Special Reports No. 2* (1932) and *No. 9* (1935)). A careful study was made of the distribution of the phosphorus in relation to

the carbon and sulphur, and a suggested explanation has been advanced to cover the mechanism of the freezing and subsequent cooling changes in the killed ingot. Certain definite observations are recorded on the structure of ingot 59, and the existence of an inter-crystalline material, believed to be a carbon-phosphorus complex, has been established in both ingots 59 and 65. This material predominates in the rim portion of ingot 59, but the authors have been unable to account for its formation and are uncertain as to whether it is a result of the rimming action or not. This point can be settled only by the examination of an ingot of similar composition but of non-rimming type. Observations on the behaviour and type of sulphide distribution in all three ingots have been made and recorded, as well as on such variations in sulphides as occur between the rim and core in ingots 59 and 65. The authors explain the incompleteness of their investigation, but consider that the detailed observations which they have made are of sufficient interest to warrant publication in view of the uncertainty as to when further work can be carried out towards its completion.

FORGING, STAMPING AND DRAWING

(Continued from pp. 14 A-16 A)

Methods and Metallurgy of Shell Manufacture. C. L. Eksergian. (Society of Automotive Engineers: Heat Treating and Forging, 1943, vol. 29, Feb., pp. 76-78, 90-92). The author discusses some of the problems involved in the forging and heat treatment of armour-piercing shell bodies. The particular advantages of induction heating are stressed. The fact that the rate of heating is reduced when the recalcrescence point of the steel is reached provides an automatic safety device which prevents excessive temperatures, for the heat is then diverted to the colder outlying layers. The width of the heated band therefore depends largely upon the time of application of the current. Similarly, for a given width of band, the greater the power input, the shorter will be the time and the steeper the temperature gradient. Improvements in the technique for welding the fins on the base of mortar cases are also described.

Forging 75 mm. and 90 mm. Shell Bodies. (Machinist, 1943, vol. 87, May 1, Armament Section). A detailed and illustrated description is given of the machinery and processes used in the manufacture of 75 mm. and 90 mm. shell bodies from solid billets. Piercing presses of the Fastraverse vertical and the Baldwin-Omes horizontal types are employed.

Improved Hydraulic Presses for Munitions Manufacture. J. H. Maude. (American Society of Mechanical Engineers: Heat Treating and Forging, 1942, vol. 28, Dec., pp. 634-638; 1943, vol.

29, Feb., pp. 80-83). The author gives details of the design and operation of oil-driven presses for mass-production munition work, in particular for making cartridge cases.

Steel Cartridge Cases for Artillery Ammunition. H. R. Turner. (Metal Progress, 1943, vol. 43, Jan., pp. 49-53). The author gives an account of the difficulties met with in developing processes for the mass production of cartridge and shell cases of steel instead of brass. Some general information on the new processes is given.

Steel Cartridge Cases Produced by Deep Drawing. H. R. Turner. (Society of Automotive Engineers: Heat Treating and Forging, 1943, vol. 29, Feb., pp. 69-72). The author describes how a process of making steel cartridge cases from one piece of sheet steel was developed. It was soon found possible by men of experience to make a case by deep drawing which would conform with the required dimensions, but the cases when fired stuck tightly in the guns. Seventy different firms were awarded experimental contracts and the methods now used for mass production represent the accumulated experience of these firms. In the method employed by fifty manufacturers a blank is cut from the sheet metal stock and this is formed into a cup. The cups are drawn by perfectly conventional methods to a cylindrical section of sufficient size to produce the finished case. This cylindrical cup is formed in tapering dies to the final shape. Machining is then applied to produce the accurate shape of the base, and excess metal at the mouth is cut off. Annealing processes are applied when necessary between certain stages of drawing to restore the metal to a condition fit for further cold work. Quenching and tempering has not been found necessary.

Bore-Grinding Tungsten Steel Cartridge Dies. E. T. Larson. (Grits and Grinds: Wire and Wire Products, 1943, vol. 18, Feb., pp. 118-119). The author describes how tungsten steel dies for drawing small-arms cartridge cases are ground internally. In most of these dies the bore is of small diameter and relatively long. Diamond resinoid wheels are used at speeds up to 25,000 r.p.m. whilst the die is revolved at 300-400 r.p.m. The feed should not exceed 0.0002 in. per pass and a traversing rate of 20-40 in. per min. is recommended.

Carbide Dies for Tube Drawing. E. Glen. (Iron and Steel, 1943, vol. 16, Apr., pp. 300-301). The author gives some particulars of "Carboloy" mandrels and dies for drawing tubes. Experience has shown that the average life of a carbide mandrel is in excess of 200,000 ft. of tubing, which is much greater than that of hardened steel or chromium-plated mandrels.

The Production of Sintered Carbides and their Application in Wire-Drawing Plants. J. Hinnüber. (Iron and Steel Institute, 1943, Translation Series, No. 142). An English translation is presented of a paper which appeared in *Stahl und Eisen*, 1942, vol. 62, Dec. 24-31, pp. 1083-1090. (See Journ. I. and S.I., 1943, No. I., p. 160 A).

New Criteria for the Selection of Diamonds for Wire Drawing Dies.

P. L. Herz. (Wire and Wire Products, 1943, vol. 18, Feb., pp. 107-114, 140, 141). The author makes recommendations on the selection of diamonds for wire drawing. He rejects the theory that the classification of diamonds according to their country of origin is also an index of their hardness. Stones with any impurity, no matter how small or how far removed from the drawing cone surface, should not be accepted for wire drawing. Other types of fault which render diamonds unsuitable for dies are: (1) Those with two of the eight crystal faces unduly enlarged; (2) stones showing single or multiple twinning; (3) dull, frosted or "corroded" stones; (4) blue-white, grey, black, milky and multi-coloured stones; (5) stones with an outer coating or envelope highly coloured in various hues whilst the crystal remains perfectly translucent; (6) those with a thick, opaque, milky or smoky "rind" or skin; most of these come from the Belgian Congo; and (7) those with a rippled or corrugated skin. Some information is given on the approximate weight of diamonds for drawing 0.014-in. wire of copper, bronze, brass and high-carbon steel.

HEAT TREATMENT

(Continued from pp. 17 A-21 A)

Thermal and Mechanical Treatment of Steel. D. Clark. (Austrian Institute of Metals: Australasian Engineer, 1943, vol. 43, Jan. 7, pp. 10-12, 45-50; Feb. 8, p. 11). The author traces the problems involved in the following five steps in the thermal and mechanical treatment of steel: (1) Casting the ingot; (2) heating preparatory to shaping; (3) mechanical manipulation; (4) cooling after mechanical manipulation; and (5) heat treatment. The differences in the heating schedules between that for a 36-in. dia. medium carbon steel ingot, that for alloy-steel ingots and that for high-speed steel are explained. The influence of rolling and forging on the grain size and orientation is dealt with. For carbon and alloy structural steel the lowest point to which mechanical work should be carried may be taken as about 75° C. above the upper critical point, and each increment of heat in excess of this will ensure less residual stress in the finished product arising from work. Examples are given in explanation of the terms annealing, normalising, spheroidising, hardening and tempering. The generally accepted theory about temper brittleness is that it is due to a change in the solubility in α -iron of some carbide-forming compound when normally cooled in the atmosphere or more slowly cooled in the furnace. Impact and hardness tests have been made with a low-alloy nickel-chromium steel and with a 1.9% manganese steel heat-treated by

quenching in oil from 840° C., tempering at 620° C. and cooling in different ways. In cases where two temperings were given, the impact values were related to the manner of cooling in the final one; in other words, the second nullifies the effect of the first.

Planning Heat Treatment by S-Curves. R. L. Rickett. (Metal Progress, 1943, vol. 43, Jan., pp. 79-81). The author explains, with examples, how the following information can be derived from the S-curve for a steel: (1) The time necessary for a measurable amount of isothermal transformation to begin, and the time necessary for transformation to become substantially complete at any particular constant temperature; (2) the type of transformation product or products formed at a particular temperature; and (3) the hardness and a conception of the other mechanical properties of the steel after transformation.

Differential Heat Treating as Applied to Band Saws. H. J. Chamberland. (Heat Treating and Forging, 1943, vol. 29, Feb., pp. 89-90). In discussing the heat treatment of band saws for cutting steel, the author points out that the longest life is obtained with saws the teeth of which are hardened down to their base, i.e., to a line just touching the bottom of the nicks. The desired depth of hardness is obtained by submitting the strip to two forms of heat treatment.

The Use of Copper in Selective Carburizing. M. M. Thompson. (American Electroplaters' Society: Metal Finishing, 1942, vol. 40, Nov., pp. 579-582). The author reports the results of tests on pieces of cold-rolled low-carbon steel strip, plated with copper in different plating solutions, to determine the plating process which offered the greatest resistance to the penetration of carbon in the subsequent carburising process. Phosphate and black oxide coatings were also tested. The following conclusions were reached: (1) The thickness of electro-deposited copper does not affect the penetration of the carburising medium provided that the coating is free from porosity; (2) the thickness of copper deposited from an acid bath must be greater than that of a coating in a cyanide or bright bath to give the same degree of protection, as the former coating is more permeable; (3) copper-lead and copper-cadmium alloy deposits give no greater protection than copper from a conventional cyanide bath; and (4) phosphate and black oxide coatings are useless as a means of preventing carburisation.

Small Tools. (Automobile Engineer, 1943, vol. 33, Apr., p. 169). Examples are given of the increased life of small tools obtained by subjecting them to the "Macrome" treatment after normal hardening and tempering. No details of the treatment itself are given.

The Transition State Theory of the Formation of Thin Oxide Films on Metals. E. A. Gulbransen. (Electrochemical Society, Apr., 1943, Preprint No. 83-4). The transition state theory of diffusion has been applied to the rate of oxidation of metals as a function of

temperature. The expression involves an entropy of activation as well as the energy of activation. Experimental results indicate that the oxidation of iron, stainless steel and copper follows the parabolic law for certain temperature and pressure ranges after a certain initial period. The difference between the oxidation rates of stainless steel and iron is shown to be due largely to an energy factor, whilst the difference between copper and iron is one of an entropy factor.

Heat Treating Machine Anneals Steel Cartridge Cases. (Heat Treating and Forging, 1943, vol. 29, Feb., p. 93). A continuous annealing furnace for heat-treating the mouth end of steel cartridge cases 37 mm. and 40 mm. in dia. is described. The cases, in the vertical position, pass on a slowly moving chain conveyor through a closely fitting refractory tunnel. In each side of the tunnel there are twelve gas burners fitted with concave ceramic heat reflectors. These burners are staggered in a zigzag line at different heights, and, as each one can be adjusted independently, the tops of the cartridge cases can be heated to any desired distance from the rim. The cases are held on rotating bases as they pass through the tunnel and this ensures a uniform distribution of heat. One case is annealed every 2 sec. and the gas consumption is remarkably low.

Atlantic Wire Company Completes Annealing Expansion. (Wire and Wire Products, 1943, vol. 18, Feb., pp. 116-117, 142). An illustrated description is given of the recently constructed annealing plant at the works of the Atlantic Wire Co. This consists of four movable gas-fired cylindrical furnaces and nine bases. For annealing coils of wire three of the bases are 62 in. in dia. and the charge can be piled to a height of 7 ft.

Cold Treatment of Metals. W. A. Phair. (Iron Age, 1943, vol. 151, Feb. 25, pp. 37-43). The author discusses the application of sub-zero temperatures for obtaining shrinkage fits in the assembly of engine parts, for "seasoning" gauges and for hardening tool steels. The advantages of shrinking the inner part, rather than expanding the outer part, to obtain a fit are that there is less possibility of altering the characteristics of the metal by cooling than by heating, the tendency to distortion is less and the handling of chilled parts is easier than that of heated parts. To obtain a larger clearance, one part can be chilled and the other heated slightly. Some data are presented on shrink fit measurements for fitting aluminium to aluminium and aluminium to steel when the outer part is heated to 300-450° F. and the inner part chilled to -35° to -40° F. Descriptions are given of a number of chilling units for the cooling of small parts to various temperatures down to -120° F.

WELDING AND CUTTING

(Continued from pp. 22 A-24 A)

Welding of Medium Carbon Steel Castings by the Metal Arc Process. S. E. Mueller, A. B. Smith and J. F. Oesterle. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 995-1027). The authors investigated the effects of preheating, welding procedure and subsequent heat-treatment on cast blocks of a plain carbon steel (carbon 0.33%) and of a manganese-molybdenum steel (carbon 0.38%, manganese 1.50%, molybdenum 0.21%). Six different types of electrodes were used to deposit metal in $\frac{3}{4}$ -in. \times $\frac{3}{4}$ -in. grooves cut across the face of the blocks which were large enough to ensure rapid dissipation of the heat. The following conclusions were drawn: (1) Casting stresses and segregation have no detrimental effect on the weldability of plain carbon steels as cast; (2) preheating is not necessary for the satisfactory welding of the above plain carbon cast steel, but subsequent annealing is desirable; (3) both preheating and a stress-relieving heat-treatment are essential for the satisfactory welding of castings of the above manganese-molybdenum steel; (4) preheating at 300° F. is far more effective in reducing the maximum hardness of the heat-affected zone than preheating at 600° F.; (5) the size or type of welding electrode has no effect on the maximum hardness of the heat-affected zone; and (6) the width of the heat-affected zone is increased by increasing the electrode size or by raising the preheating temperature.

The Common Mechanical Properties of Carbon-Steel Weld Metal in Electric Arc Welding. O. T. Barnett. (Welding Journal, 1943, vol. 22, Feb., pp. 108-113). The author reviews the results of tests in which the effects of different electrode diameters and welding procedures on the yield point, tensile strength and elongation of the deposited weld metal were studied. In general, increasing the electrode diameter slightly decreased the yield point and tensile strength, the elongation remaining practically the same. The effect of weaving from one plate edge to the centre of the welding space and thus depositing twice as many beads, instead of weaving across the full width, was to increase slightly the yield point, tensile strength and elongation. Some of the standard tests for welding electrodes worked out by the American Welding Society and the A.S.T.M. are briefly described.

An Investigation of the Behaviour of Residual Stresses under External Load and their Effect on Safety. J. T. Norton and D. Rosenthal. (Welding Journal, 1943, vol. 22, Feb., pp. 63-S-78-S). The authors describe an investigation of the residual stresses in flat steel plate, containing 0.17-0.18% of carbon, after the application of local heat supplied by pressing the specimen between the ends of two round mild steel electrodes and applying currents in the 3000-

4000-amp. range for different periods of time. The effects of subsequent static, dynamic and fatigue tests on the residual stresses were also studied. The specimens measured 3 in. \times 15 in. and the thickness varied between 0.168 and 0.3 in. The residual stresses were gradually relieved by static loading in tension; this relief was not limited to the zone of high residual tension, but extended over the whole area affected by the residual stresses. The removal of the applied load, subsequent reloading to the same amount and changing the duration of the load did not change the extent to which the residual stresses were relieved. Further relief occurred only when the external load was increased. The general feature of the relief of residual stress as found in static tension was confirmed in static bending. It was concluded that in bending, the inner and less stressed layers of the specimen tend to restrict the plastic flow of the outer layer; if this is so, bending is less effective than direct tension as a means of relieving stress. In the fatigue tests the specimens were subjected to reversed bending at their natural frequency by means of electromagnets acting at both ends. After establishing the fatigue limit of stress-free specimens, three specimens with residual stresses were vibrated as follows: (a) At below and at the fatigue limit of the stress-free specimens; (b) at and slightly above this fatigue limit; and (c) at and well above this fatigue limit. The tests were interrupted after various periods of time to investigate the behaviour of the residual stress under fatigue. The X-ray diffraction method failed to disclose any influence of the repeated loading on the relief of the residual stress. The redistribution of the stress accomplished after the first cycle seemed to undergo no further change no matter how often the same cycle was repeated, even if the applied load was close to the fatigue limit of the specimen.

Anchor Chains Are Now Electric Welded by Unionmelt Method. H. W. Young. (Steel, 1943, vol. 112, Jan. 18, pp. 85-86, 96). The author describes a process of manufacturing steel anchor chain from $2\frac{1}{16}$ -in. dia. bars, which has been developed by the Pacific Chain and Manufacturing Co. The bars are heated and bent into links in a forming machine; each bar is passed through the preceding link so that a continuous chain is formed. The forming machine leaves a V-shaped gap between the bar ends at the side of each link. This chain is hauled up a conveyor and the alternate links which are in the vertical position are welded by the Unionmelt process in a machine with special jaws to fit the links (see Journ. I. and S.I., 1939, No. I., p. 284 A). The chain is then turned 90° and the intermediate links welded. There are four welding machines each with a capacity of 40 links per hr. The process is controlled so that only two machines are taking welding current at one time.

Alloy Steels for Welding. H. W. G. Hignett. (Journal of the West of Scotland Iron and Steel Institute, 1942-43, vol. 50, Part III., pp. 27-34). After reviewing the literature on tests relating to the hardness of a steel after cooling at different velocities to its weld-

ability, the author shows how the Davenport and Bain **S**-curves can be applied to study weldability. In the case of alloy steels, the phenomena resulting from continuous cooling, as shown by time-temperature or dilatometric curves, may be more complex than for carbon steels. A third change point Ar'' may appear, intermediate between Ar' and Ar''' . In addition to displacing the **S**-curves to the right, alloying elements distort them in various ways, so that if the pearlite transformation is suppressed by rapid cooling, it is no longer certain that transformation will not occur until the martensite range is reached. It is also possible to depress the "nose" of the **S**-curve in such a way that at rates of cooling, such as are experienced in normalising, transformation is induced to take place initially at a lower temperature than in the case of the plain carbon steels, with consequent production of fine structures and correspondingly high yield points in the normalised condition. This indicates a possible means of producing a high yield-point steel which will not give unduly high hardness in the heat-affected zones of a weld. Such a steel has been developed. It contains carbon 0.185%, nickel 1.97%, chromium 0.25% and molybdenum 0.27%. Its yield point is 30 tons per sq. in. and it can be welded without special precautions in the as-rolled or normalised condition.

Swiss Standards on Weldability of Steel. (Journal de la Soudure : Welding Journal, 1943, vol. 22, Feb., pp. 94-S-96-S). Particulars are given of weldability tests adopted in two standards issued by the Welding Committee of the Standards Bureau of Switzerland.

Weldability of NE 8630 Steel for Aircraft Structures and a Suggested Specification for Weld Metals. A. R. Lytle and K. H. Koopman. (Welding Journal, 1943, vol. 22, Feb., pp. 82-S-93-S). The authors report the results of tests of the weldability, as determined by hardness and bend tests, of National Emergency steel 8630 as compared with that of steel S.A.E. X-4130. Both of these are 0.30%-carbon low-alloy steels used in aircraft construction. Steel NE 8630 contained chromium 0.49%, nickel 0.71% and molybdenum 0.17%. Steel X-4130 contained chromium 0.99%, no nickel and molybdenum 0.19%. The weldability of NE 8630 steel sheet was found to be at least equal to that of S.A.E. X-4130 steel in the thicknesses tested. The authors suggest a specification with minimum tensile and bend test values for deposited weld metal which would lead to a satisfactory balance between the physical properties of the weld and base metals in the oxy-acetylene welding of the new steel.

Reclaiming Worn Parts. (Automobile Engineer, 1943, vol. 33, Apr., pp. 165-168). Examples are given of the manner in which worn and broken parts of motor vehicles at the road transport department of the London Midland and Scottish Railway Co. are repaired. On the basis of experience, one of three basic methods is employed, namely, metal spraying, electro-chemical deposition and welding.

The "Redux" Process. (Engineer, 1943, vol. 175, May 14, p. 395). Brief details are given of a process, which provides, by the use of synthetic-resin adhesives, a method of bonding light alloys and steel with a strength stated to exceed that of riveting, and of giving strong joints between metal and wood. It is called the "Redux" process. The joint is without stress concentrations and can be made aerodynamically smooth and petrol-tight. The adhesives used are also unaffected by water and oil. The process is economical and lends itself to modern production methods. The resin bond is mildly thermoplastic and loses strength at temperatures above 100° C.; the loss of strength is, however, regained on subsequent cooling, provided that the joint has not been subjected to undue strain. The process works best with trivalent metals such as aluminium, chromium, iron or steel and gives less satisfactory joints with brass, tin or zinc.

Improved Methods of Machine Flame-Cutting. H. E. Rockefeller. (Welding Journal, 1943, vol. 22, Feb., pp. 93-99). The author describes and illustrates several types of machine for the oxy-acetylene cutting of steel plate with special reference to methods of preparing plate edges for welding. Some machines have up to three nozzles in close sequence with which "multiface" cutting can be carried out.

PROPERTIES AND TESTS

(Continued from pp. 30 A-34 A)

Tessellated Stresses.—Part II. F. László. (Iron and Steel Institute, 1943, this Journal, Section I). Continuing his study of tessellated stresses (*see* Journ. I. and S.I., 1943, No. I., p. 61 A), the author, in Part II., discusses results of recent investigations of structural tessellated stresses in materials consisting of components with different elastic constants, with special reference to cast and malleable iron. The question of strain energy due to tessellated stresses is considered, with particular regard to phase transformation. Tessellated stresses in the free surface are carefully analysed and their possible rôle in connection with damping and surface deficiency in fatigue is pointed out.

The Creep Strength of Steel at Room Temperature. A. Krisch. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 539-542). The author reports the results of creep tests at room temperature on specimens of two ordinary carbon steels, one low-chromium molybdenum steel, a steel containing chromium 14.8% and nickel 0.22%, and an 18/8 stainless steel containing 0.20% of molybdenum. Static loads exceeding the elastic limit of the steel at room tempera-

ture were applied and time-extension curves were obtained. With the 0.13%-carbon steel there was no extension after 5 hr.; with the 0.23%-carbon steel the extension curve became horizontal after about 100 hr. In the case of the three alloy steels the extension still continued after 400 hr.

The "Hyglo" Crack-Detection Process. (Engineering, 1943, vol. 155, Apr. 30, p. 357). A brief description is given of a method of detecting cracks and flaws in the surface of metals, plastics and ceramic materials. The part is dipped in a fluorescent liquid and then examined under ultra-violet light. In this process, called the "Hyglo" system, the washing procedure after immersion is no longer necessary as it is sufficient to allow the parts to dry in a wire basket for about half a minute while the solution partly evaporates and partly drains back into the tank.

The Importance of "Grain" in Steel. (Heat Treating and Forging, 1943, vol. 29, Feb., pp. 73-75). In this brief article, prepared by the technical staff of the Allegheny Ludlum Steel Corporation, information is given on the principal characteristics of fine, medium and coarse-grained steel. Coarse-grained steels can be hardened to a greater depth and have a higher creep strength than fine-grained steels.

The Effect of the Degree of Reduction by Forging on the Bending-Fatigue Strength of Low-Alloy Steel Parallel and at Right Angles to the Forging Direction. H. Krainer. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 543-546). The author reports on an investigation of the effect of the degree of reduction by forging on the fatigue strength of specimens cut in the longitudinal and transverse directions from a bar of forged and heat-treated steel containing carbon 0.32%, chromium 0.2% and nickel 1%; the results are compared with those given in the literature for a chromium-manganese-molybdenum-vanadium steel and a chromium-nickel-molybdenum steel. With specimens cut in the longitudinal direction, the ratio of fatigue strength to tensile strength of both smooth and notched specimens decreases with increasing reduction by forging, and the notch sensitivity increases. With specimens cut in the transverse direction, the above ratio also decreases with increasing reduction, but in this case the reduction does not appear to affect the notch sensitivity. The ratio of the fatigue strength in the transverse direction to that in the longitudinal direction of both smooth and notched specimens decreases with increasing reduction, and the fall in the value of this ratio is greater for smooth specimens than it is for notched ones.

End-Quench Test and Its Application. W. E. Jominy. (Metal Progress, 1943, vol. 43, Jan., pp. 77-79). The author discusses the adoption of standard methods of making end-quench hardenability tests and how to present and compare the data obtained. Some hardenability curves are presented for National Emergency steels 8620, 8630, 8739 and for S.A.E. steel 4130.

Shop Performance of NE Steels. G. C. Riegel. (Metal Progress, 1943, vol. 43, Jan., pp. 82-83). The author relates some experience, at a works manufacturing tractors, concerning the properties and suitability of some of the 8000 series of National Emergency steels after heat treatment.

Properties of NE Steels at Room and Subnormal Temperatures. J. H. Jones. (Metal Progress, 1943, vol. 43, Jan., pp. 83-85). The author presents data on the mechanical properties at room temperature and at temperatures down to -65° F. of some of the 8000 and 9000 series of National Emergency steels.

Carburizing Grades of NE Steels. T. A. Frischman. (Metal Progress, 1943, vol. 43, Jan., p. 86). The author describes the carburising characteristics of the chromium-nickel-molybdenum National Emergency steels of the 8600, 8700 and 8800 series.

Heat Treating for Machinability. L. E. Webb. (Metal Progress, 1943, vol. 43, Jan., pp. 87-89). Some micrographs and data are presented showing the structure and properties obtaining after heat-treating the National Emergency nickel-chromium-molybdenum steels 8620 and 8722.

User Report No. 8 on Experience with NE (National Emergency) Alloy Steels. B. B. Wescott. (Steel, 1943, vol. 112, Jan. 18, pp. 66-69). The author presents test data on some of the 8000 series of National Emergency Steels which have been successfully used in the United States for oil-well drilling.

Applications of the New Cast Irons. C. S. Darling. (Mechanical World, 1943, vol. 113, Mar. 26, pp. 334-337; Apr. 2, pp. 354-357; Apr. 9, pp. 393-396). The author reviews the properties of some of the high-strength cast irons, particularly Meehanite. Tables and curves are presented showing: (a) The oxidation and growth of plain and austenitic cast irons after up to 40 cycles of heating to 1500° F. and cooling; (b) the growth of plain and nickel cast irons after up to 40 cycles of heat treatment in an oxidising atmosphere; (c) the stress-strain curve for Meehanite in the as-cast state; (d) the increase in the tensile strength of Meehanite obtained by quenching and tempering; (e) the results of tensile, hardness, impact and torsional fatigue tests on five materials for automobile engine crankshafts, viz.: a low-alloy nickel-chromium-molybdenum steel, a copper-chromium iron, an inoculated high-strength iron, a chromium-molybdenum iron and a low-alloy nickel-chromium iron; (f) the damping capacity of a number of cast irons and a carbon steel; and (g) the applications of a number of high-duty cast irons with analyses and physical properties.

Ball Wear in Cylindrical Mills. T. K. Prentice. (Journal of the Chemical, Metallurgical and Mining Society of South Africa, 1943, vol. 43, Jan.-Feb., pp. 99-116). The author gives an account of an investigation, lasting fifteen months, of the wear of steel balls in a cylindrical ball mill used for grinding ores in the Transvaal gold mining industry. The mill used for the tests was 30 in. in dia. and

17 in. long. Sets of balls 3 in. and $2\frac{1}{2}$ in. in dia. were run continuously for periods of 5 days $13\frac{1}{2}$ hr. each, the mill being revolved at 30.5 r.p.m., after which the reduction in volume of the balls was determined; from this the number of days taken to reduce the diameter to 1 in. was calculated. The steel balls with the longest life were forged and contained: Carbon 0.90%, manganese 0.89%, chromium 0.8–1.0%, with silicon, sulphur and phosphorus not exceeding 0.22%, 0.035% and 0.025% respectively; the hardness was 350–400 Brinell. The tests showed that the rolled balls with the best durability contained in all cases carbon 0.60–0.90%, chromium 0.85–2.1% or about 2.5% of manganese.

In the second part of the paper a statistical analysis of the test results is made and from this a theory for the wear of balls in grinding mills is developed. The tests disclosed that while wearing down from 3 in. or $2\frac{1}{2}$ in. to $1\frac{1}{4}$ in. in dia. the loss of weight was directly proportional to the square of the diameter and therefore to the surface area of the ball; the subsequent wear from $1\frac{1}{4}$ in. downwards was relatively slower and more in accord with E. W. Davis' theory that the loss in weight is directly proportional to the cube of the diameter.

METALLOGRAPHY AND CONSTITUTION

(Continued from p. 34 A)

Wartime Metallurgy Conserves Strategic Materials. Part VI. Grain Size. R. E. Orton and W. F. Carter. (Machine Design, 1943, vol. 15, Jan., pp. 59–62). Continuation of a series of articles (see Journ. I. and S.I., 1943, No. I., p. 206 A). The authors consider how grain size affects the properties of steel and describe how grain size is measured. The impact strength of a steel increases rapidly with decreasing grain size. Coarse-grained steel has a better resistance to the initiation of a fatigue crack, whilst fine-grained steel has a better resistance to the spreading of a crack once it has formed. Decreasing the grain size lowers the hardenability. The grain size can be controlled by the addition of materials which form insoluble carbides, and the larger the number of carbide nuclei the finer will be the size of the grains and the less their growth.

Radiographic Inspection Technique Applied to Special Welding Problems. D. M. McCutcheon. (Welding Journal, 1943, vol. 22, Jan., pp. 16–20). The author describes some methods of using a 1000 kV. X-ray installation for examining welds in steel plates and castings, and spot welds in aluminium.

Constitution of the Iron-Tin Alloys. O. E. Romig. (Metal Progress, 1942, vol. 42, Nov., pp. 899–904). With the increasing proportion of tinplate in the scrap charged into steel furnaces the

solubility of tin in iron is of increasing interest. In this paper the author reviews the literature on the iron-tin system and reproduces iron-tin constitutional diagrams as constructed by various research workers.

CORROSION OF IRON AND STEEL

Caustic Embrittlement. E. W. Colbeck, S. H. Smith and L. Powell. (Proceedings of the Institution of Mechanical Engineers, 1943, vol. 149, pp. 63-73). The authors describe an investigation of the caustic embrittlement of steel using an apparatus similar to that of G. Straub and T. A. Bradbury (*see* Journ. I. and S.I., 1938, No. II., p. 403 A). In this, the solution to be tested is contained in a hollow sealed tubular specimen, which is heated to any desired temperature in the steam boiler range, and subjected to a tensile load by means of a spring. It has not been possible to reproduce the results claimed by Straub, but a number of examples of intergranular cracking have been produced. Some of these have been obtained when using dilute solutions containing amounts of sodium hydroxide and silicate such as would be found in boiler waters. There is evidence that embrittlement occurs more readily in poor quality steel and under conditions of non-uniform stress distribution, but it has not been possible to reproduce results with any degree of certainty. Failures and cracking which have occurred appear to fall into two classes; the first is a true intercrystalline attack, the cracks being fine, numerous and free from oxide, and usually associated with a crystalline black deposit of magnetic iron oxide in the bore of the specimen. The second class takes the form of fissuring of the attacked surface; the fissures are usually straight and blunt-ended; they are transcrystalline, often filled with products of corrosion, and may extend in the form of transcrystalline cracks, few in number, also filled with products of corrosion. The second form of attack is not considered to be genuine caustic embrittlement, though it is obviously of importance. A survey is made of the more important literature on caustic embrittlement published between 1935 and 1941.

Caustic Embrittlement. D. Brownlie. (Steam Engineer, 1943, vol. 12, Mar., pp. 162-164, 174). The author describes the Straub and Bradbury embrittlement detector used by Colbeck, Smith and Powell in their recent investigation of caustic embrittlement. The opinion that embrittlement in boilers becomes more troublesome as the pressure increases has little or no foundation in fact. He also discusses the conclusions of Andrew, Bose, Lee and Quarrell (*see* Journ. I. and S.I., 1942, No. II., p. 203 P) regarding the formation of hair-line cracks.

Thermodynamic Considerations in the Corrosion of Metals. J. C. Warner. (Electrochemical Society, Apr., 1943, Preprint No. 83-5).

The author discusses how thermodynamic data can be applied to the study of corrosion reactions. The available data are used to calculate the spontaneity of corrosion reactions for most of the common metals in de-aerated water and in water saturated with air containing no carbon dioxide. If the corrosion process occurs by an electrochemical mechanism, the maximum potential of the corrosion couple may be calculated; the results of such calculations are summarised for the common metals in several ordinary environments. A method analogous to the application of Bernoulli's theorem to fluid flow problems has been used to define the condition for the steady state limiting corrosion rate.

The Corrosion of Iron and Steel and Problems of Prevention. V. C. J. Nightingall. (*Journal of the Institution of Engineers Australia*, 1942, vol. 14, Nov., pp. 253-258). After explaining the electrolytic theory of corrosion the author discusses how the progress of corrosion is affected by pickling, differential aeration and polarisation. Notwithstanding the excellent results obtained in commercial pickling, a piece of steel plate examined under a low-power microscope is found to have numerous very fine particles of black oxide embedded in it, and these only require an electrolyte, such as water, to start corrosion. When all mill-scale has been ground off, galvanic couples can be set up by differential aeration from any aqueous electrolyte. A process of cathode protection has been developed which consists of fixing zinc in powder form to a chemically prepared iron or mild steel surface in such a manner that some of the zinc is embedded in a silicate of zinc matrix of high electrical resistance, which is sufficient to prevent the short circuiting of at least some of the zinc held in the matrix to the iron or mild-steel surface. Not much is known regarding the mechanism of the attachment to the iron surface; the action takes place immediately, and the zinc coat is firmly fixed after heating to 230-250° F. for 10 min., after which the main body of the zinc silicate adheres to the zinc and iron surface. The coating acquires a secondary hardness after about one month's weathering. The cathodic reduction of mill-scale has led to the successful development of a process for the reduction of scale or rust existing on mild-steel surfaces where water is constantly present (e.g., water-cooled roofs to petrol tanks in hot climates). In this, the first coat is employed to reduce scale and rust by the action of hydrogen; this action is allowed to continue for 12 to 18 months, when the scale and rust are reduced sufficiently to brush the surface down with a steel brush. Another coat is then applied and the treatment continued twice in three years, after which it is found that no further corrosion takes place.

Preventing Internal Corrosion of Pipe Lines. A. Wachter and S. S. Smith. (*Industrial and Engineering Chemistry, Industrial Edition*, 1943, vol. 35, Mar., pp. 358-367). The authors study the prevention of the internal corrosion of petrol pipe lines with special reference to the inhibiting properties of sodium nitrite. A test

procedure was devised in which 6-in. rods of polished low-carbon steel were fixed in 4-oz. oil-sample bottles containing a mixture of petrol and water with an air space of about 30 ml. The bottles were placed in a rotating machine which turned them end over end at 60 r.p.m. The air space was replenished every two days, and the duration of the tests was usually 14 days. The loss in weight, after carefully cleaning the rods, was determined. Samples of water used for these tests were taken at various places along a 450-mile petrol pipe line. The point of sampling had no influence on the rate of corrosion. Water samples tested under identical conditions, but with an addition of 0.1% by weight of sodium nitrite, did not attack the steel rods, which remained bright all over. It was necessary for the water to have an initial pH value greater than 6 for the sodium nitrite to inhibit corrosion completely. Sodium nitrite was found to be equally effective in preventing the corrosion of steel by petroleum, fuel oil and Diesel oil. In two years' operation of a 450-mile pipe line no adverse effect of the inhibitor on the product flowing through it has been observed.

Laboratory Tests on the Progress of Corrosion of Steel Plate Alternately in Contact with Water and Petrol. J. Morsing. (Iron and Steel Institute, 1943, Translation Series, No. 132). This is an English translation of a paper which appeared recently in Statens Provvningsanstalt, 1942, Report No. 87, pp. 3-35. (See Journ. I. and S.I., 1943, No. I., p. 66 A).

ANALYSIS

The Use of the Spectrograph as an Aid in Improving Open Hearth Practice. J. A. Sample. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1942, vol. 30, Aug., pp. 875-876). The author describes the benefits accruing from the use of a spectrograph to make determinations of the copper, tin and chromium in heats of steel sufficiently rapidly for corrective measures to be applied before tapping time. This is of increased importance at the present time, when large quantities of light scrap are being used.

Quantitative Spectrographic Analysis of Stainless Steels. M. F. Hasler, C. E. Harvey and H. W. Dietert. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, Feb., pp. 102-107). A spectrographic method of analysis is described with which rapid and accurate quantitative analyses of all the metallic constituents in stainless steel can be made. A direct-current arc and a specially shaped carbon electrode enable the chromium and nickel to be determined with an accuracy of 2%. Full details of the procedure are given.

New Methods for the Separation of Nickel and Cobalt from Iron and of Nickel from Cobalt. B. S. Evans. (*Analyst*, 1943, vol. 68, Mar., pp. 67-70). The author recommends the use of potassium cobalticyanide for the separation of nickel and cobalt from iron. This is oxidised to the tervalent state (by means of nitric acid) before the addition of the reagent, so as to prevent co-precipitation. The precipitate is decomposed by treatment with sodium hydroxide and hydrogen peroxide, and the hydroxides formed are dissolved in hydrochloric acid. In aliquote parts of the solution obtained the sum of nickel + cobalt as well as nickel alone are determined cyanometrically, cobalt being estimated by difference. In conclusion the author recommends a method for the determination of nickel and cobalt in one solution, nickel being precipitated by dimethyl glyoxime after transformation of cobalt into cobalticyanide.

Perchloric Acid Method for Determination of Silicon in Ferro-silicon. L. Waldbauer and S. O. Rue. (*Industrial and Engineering Chemistry, Analytical Edition*, 1943, vol. 15, Feb., p. 131). The authors describe a simplified method for the determination of silicon in samples of ferro-silicon containing from 25% to 75% of silicon. The sample is fused with a mixture of sodium peroxide, sodium carbonate and sodium perchlorate; the melt is then decomposed with water and hydrochloric acid, and the silicic acid formed is dehydrated with perchloric acid. A correction factor is introduced to eliminate the necessity for a second dehydration.

Microdetermination of Carbon in Steels. E. W. Balis, H. A. Liebhafsky and E. H. Winslow. (*Industrial and Engineering Chemistry, Analytical Edition*, 1943, vol. 15, Jan., pp. 68-69). The authors describe an apparatus and procedure which they developed for determining with great accuracy the amount of carbon in low-carbon steel and in Nichrome. The apparatus is a modification of the standard carbon-hydrogen train. In a 100-mg. sample of steel 0.1% of carbon can be determined within $\pm 0.003\%$. The method is particularly useful where only a few samples are to be analysed at rare intervals.

The Rapid Photoelectric Determination of Cobalt in Steels using Nitroso-R-Salt. F. W. Haywood and A. A. R. Wood. (*Journal of the Society of Chemical Industry*, 1943, vol. 62, Mar., pp. 37-39). The use of nitroso-R-salt as a specific reagent for the determination of cobalt in steels is described. Full development of the coloured cobalt complex is obtained when all mineral acid ions are neutralised by means of sodium acetate. Other interfering elements occurring in steels, while producing complexes with nitroso-R-salt, are completely destroyed in an excess of nitric acid, the cobalt complex being unaffected. Based on these investigations a method has been devised which gives speedy, accurate and reproducible results.

Electrographic Detection of Molybdenum in Steel Alloys. J. A. Calamari, R. Hubata and P. B. Roth. (*Industrial and Engineering Chemistry, Analytical Edition*, 1943, vol. 15, Jan., p. 71). The

authors describe a test by means of which the presence of molybdenum in steel can be detected in a few seconds. A wad of filter-paper moistened with sodium nitrate solution is placed on the test-piece, which is made the anode, and a graphite cathode is pressed against the free side of the wad for about 1 sec. while a current of 0.5–1.0 amp. at 6–9 V. is passed. The moistened end of the filter-paper is washed in lead-acetate solution to precipitate the molybdate. A few drops of a hydrochloric-acid solution of stannous chloride and potassium thiocyanate are put on the side of the filter-paper which was adjacent to the metal, and the trivalent molybdenum thiocyanate which forms yields a carmine red stain.

Rapid Analysis of Oxygen in Molten Iron and Steel. G. Derge. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1544: Metals Technology, 1943, vol. 10, Jan.). The author describes a sampling technique which was developed for making oxygen determinations of a heat of steel sufficiently rapidly to be used for control purposes. A split wedge-shaped copper mould is employed; this chills the sample so rapidly that it can be removed at once with the bare hands. A small piece is cut off the bottom of the wedge for analysis and placed in a previously heated and evacuated vacuum-fusion apparatus; the evolved gas is collected, and, after the operator has measured its volume, he can read off the amount of oxygen from a chart which incorporates the necessary corrections. The determination requires not more than 10 min. from taking the sample. The apparatus is described and illustrated.

BOOK NOTICE

BREARLEY, H. "*Knotted String—Autobiography of a Steel-Maker.*" 8vo, pp. ix + 198. London, 1941: Longmans, Green & Co. (Price 10s. 6d.)

Brearley has been busy again, this time with scenes from his life. These are portrayed with wit, brilliance and faithfulness that would have been possible to no other writer of the story. Posterity is the richer for this little book.

The first two chapters give us a first-hand view of family life in industrial Sheffield fifty years ago. Brearley has the gift of making his reader see, feel and hear with him whatever he describes. There are rapid changes of scene and subject, full of interest. Intimate pictures of life and associations of steel workers include crucible steel melting, file cutting, iron puddling and others.

The author's early experiences as a laboratory assistant make pleasant reading. Some of his views on education will not find general acceptance. Most readers will, however, agree that education for citizenship has suffered under bureaucratic control. There is sound sense in the author's plea for the rational use of data on the effect of impurities in steel and for a keen spirit of enquiry in the metallurgist's outlook. It is important to know how and why things happen in steel furnaces. Best results are obtained when troubles are brought to the notice of

experienced workmen. When the steel is wrong we must let the men know. We are sternly warned of the dangers of second-hand knowledge, superficial information and rumour-mongering; of the perils of directors' boards having no steelmaker on them.

The chapter on stainless steel is very interesting, but rather "knotted" for easy assimilation of the more intimate features. It is a pity that the early history of stainless steel was so "knotted". No less interesting are the parts dealing with life in a Russian steel colony and with the author's work with Brown Bayleys.

Brearely is very appreciative of his inspiring tutor in the analytical laboratory, and of the assistance of his scores of friends with "hard hands and black faces" to whom he referred when he received the Bessemer Medal in 1920.

H. SUTTON.

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MINERAL RESOURCES

Replacement Hematite Deposits, Steep Rock Lake, Ontario. H. M. Roberts and M. W. Bartley. (American Institute of Mining and Metallurgical Engineers: Technical Publication No. 1543: Mining Technology, 1943, vol. 7, Jan.). The presence of three substantial red and brown hematite zones in the bed of Steep Rock Lake, Ontario, about 140 miles west of Port Arthur on Lake Superior, has been established by drillings. An account of the geology of the region is given. It is considered practicable to divert the waters flowing into Steep Rock Lake and to develop open pits on the upper part of two of the large ore bodies by damming off and pumping out the water in the part of the lake in which they occur. The ore contains about 60% of iron.

The United Nations' Newest Source of Iron. A. Malozemoff. (Engineering and Mining Journal, 1942, vol. 143, Dec., pp. 55-59; 1943, vol. 144, Jan., pp. 56-59). After a brief review of the world sources of supply of iron ore, the author describes the geology, location and methods of mining the rich Itabira iron ore in Brazil. An agreement has recently been reached between the United States, Great Britain and Brazil under which an output of about 600,000 tons per annum will be divided equally between the United States and Great Britain. An account of this ore field was recently given by E. A. Teixeira (*see* Journ. I. and S.I., 1943, No. I., p. 37 A).

Some Properties of National Zirconium Ores. F. B. Angeleri. (Anais da Associação Química do Brasil, 1942, vol. 1, Oct., p. 225, Reprint). The author discusses the zirconium ore deposits of Brazil, which he believes to be the largest and richest in the world, and describes some tests of the refractory properties of the ore. Samples from the Caldas plateau contained 73-79% of ZrO_2 . Samples which were fired at 1400° and 1500° C. were tested under a load of 2 kg. per sq. cm. and the initial softening temperature was 1580-1590° C. This mineral is used in Brazil instead of magnesite for lining small electric furnaces. The refractories made with it are at present not of high quality, but the author believes bricks of better quality could be made without the addition of binding agents.

ORES—MINING AND TREATMENT

(Continued from p. 1 A)

Lake Superior Iron Ore and the War Emergency. E. W. Davis. (Blast Furnace and Steel Plant, 1942, vol. 30, Dec., pp. 1364-1368; 1943, vol. 31, Feb., pp. 211-216). The information in this paper is

released for publication by the Iron and Steel Branch of the United States War Production Board. Statistics are presented on the quantities of iron ore from the Lake Superior district obtained by open working and underground mining, the quantities of concentrate produced, the estimated reserves and probable future requirements. The author recommends measures to be taken by the United States Government and by the State of Minnesota with a view to encouraging the production and smelting of low-grade taconite ore and preventing the high-grade open-pit ore of the Mesaba Range from being worked out too rapidly.

Development in the Methods of Mining and Treating Iron Ores. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 84-87). A summary is given of the development of mining and ore-treatment methods on the Mesaba Range. The system of transport from the mine to the washing plant has developed from steam locomotives to Diesel lorries and electrically driven conveyor belts. Electric shovels of from 2 to 6 cu. yd. capacity form the standard method of loading. Lighter rock is separated from the ore in a high-density medium of a suspension of finely ground 15% ferro-silicon in water. A method has been developed, which only awaits a full-scale plant test, to treat magnetic taconite of which there are immense reserves in the Mesaba Range.

Youngstown Sheet and Tube Now Making Sinter at Campbell Works. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 109-112, 118). An illustrated description is given of the new sintering plant at the Campbell Works of the Youngstown Sheet and Tube Company. (See Journ. I. and S.I., 1943, No. I., p. 189 A).

Modern Sintering Plant Handles Fine Ores and Flue Dust. (Steel, 1943, vol. 112, Mar. 1, pp. 102-105, 139-140). An illustrated description is given of the plant and process for the sintering of ore-fines and blast-furnace flue dust at the Campbell Works of the Youngstown Sheet and Tube Co.

REFRACTORY MATERIALS

(Continued from pp. 1 A-3 A)

Developments in Steel Plant Refractories. C. A. Brashares. (Iron and Steel Engineer, 1943, vol. 20, Feb., pp. 48-52). The author discusses the properties and applications of super-duty silica, alumina and fireclay bricks. Corundum refractories of the 90%-alumina type are used in piers, supporting arches and other constructions where loads are carried at very high temperatures. An increase of the gas pressure in a furnace causes a very great increase in the loss of weight of bricks by spalling. The difference

in the properties of machine-made standard sizes and of hand-made shapes of the same material remains very marked because de-airing can be applied to the former but not to the latter.

High Temperature Resistivity Measurements on Compressed Granular Refractory Materials. G. H. Fetterley. (Electrochemical Society, Apr., 1943, Preprint No. 83-2). The author describes a quick and inexpensive method of determining the electrical resistance of compressed granular refractory materials at temperatures up to 1000 C°. The accuracy is sufficient for commercial control purposes. The leakage resistance of tubular heating elements insulated with periclase was found to be proportional to the resistivity coefficient of the grains used for insulation. The theoretical derivation and method of calculation of this factor are explained.

Casting Pit Refractories as a Source of Non-Metallic Inclusions in Steel. J. R. Rait. (Transactions of the British Ceramic Society, 1943, vol. 42, Apr., pp. 57-90). The failure of a high percentage of forgings to meet the transverse elongation requirements was thought to be due to an increase in the non-metallic inclusions of the slaggy stringer type, and, as this was coincident with the use of more siliceous refractories for the uphill casting, a systematic investigation of uphill casting-pit refractories as a source of non-metallic inclusions was made. The following conclusions were reached: (1) The manganese of the liquid steel reduces the free silica, particularly the quartz of the refractory, to produce MnO and silicon in an endeavour to reach equilibrium, since the manganese/silicon ratio of the steel is greater than the equilibrium value. The MnO thus formed fluxes the refractory to form a liquid manganese alumino-silicate slag. The amount of slag formed on the more siliceous refractories is very much greater than on the aluminous refractories (Al_2O_3 38%); this great difference in attack is attributed to the large quartz content of the former type and the very low content or absence of quartz in the latter. (2) The manganese alumino-silicate slag is washed off the runner bricks and carried into the ingots. In the case of small 11-in. ingots, freezing is sufficiently rapid to trap some of this slag. A greater amount of this slag is introduced and retained in the ingots from the more siliceous refractories. (3) During forging, these manganese alumino-silicates are plastic and are deformed into stringers. In the case of forgings of steel poured through the siliceous refractories there are sufficient stringers to lower the transverse elongation. (4) The composition and amounts of slag formed on a given type of refractory by different alloy steels with similar carbon, manganese and silicon contents are very similar; thus, the alloying constituents have little influence on this reaction. A steel with a higher manganese content and manganese/silicon ratio produces a slag with a higher MnO content on a given refractory. (5) The compositions of the manganese alumino-silicate slags formed on uphill refractories by the action of various steels with similar carbon,

manganese and silicon contents fall within a small area in the $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$ ternary diagram. The line from MnO through the composition of the slag intersects the $\text{Al}_2\text{O}_3\text{-SiO}_2$ side of the diagram at the approximate composition of the firebrick from which it is derived. (6) The composition of the slaggy inclusions is therefore controlled by the carbon, manganese and silicon contents of the steel and the composition of the refractories. (7) The crystallisation paths of these slags can be obtained from the ternary $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$ diagram recently published by R. B. Snow (*see* p. 1 A). The extent to which crystallisation is completed is governed by the subsequent heat treatment of the ingots. (8) Manganese aluminosilicate inclusions in steel are derived from uphill refractories and tundish linings, and it is also highly probable that any firebrick material with which the steel comes in contact is a possible source of these non-metallic inclusions. (9) These manganese aluminosilicates also occur on ingot surfaces. (10) The constitution and properties of the refractories are extremely important. The manganese attack is greatly reduced when quartz is absent, which normally requires a minimum alumina content of 38%. Fireclay refractories should be fired at a minimum temperature of 1100°C. to attain the minimum free silica content. The maximum on the spalling-resistance/firing-temperature curve should occur at 1100°C. or higher, so that the maximum or adequate spalling resistance can be achieved with the minimum free silica content. (11) Although inclusions due to spalling of the refractories were not detected in this investigation, it is considered that spalling is a possible source of this trouble, but such inclusions would be fairly large and would retain the characteristics of the firebrick. (12) It has been found in various steelworks that fireclay nozzles which have been boiled in tar have an increased resistance to wear. The most probable explanation is that the free carbon deposited in the pores of the nozzle decreases the manganese reduction of silica, and the evaporation of the volatile fractions of the tar tends to maintain the nozzle at a lower temperature.

FUEL

(Continued from pp. 35 A-36 A)

A Study of Carbon Combustibility by a Semi-Micro Method. H. E. Blayden, H. L. Riley and F. Shaw. (*Fuel in Science and Practice*, 1943, vol. 22, Mar.-Apr., pp. 32-38; May-June, pp. 64-71). The authors give an account of a semi-micro method which they devised for determining the ignition temperature of carbon and of a comprehensive study of the factors influencing carbon combustibility, with special reference to the alkali activation

of carbon combustion. The apparatus used for determining the ignition temperature of 0.25-g. samples is described in detail. Carbon was prepared from pure cellulose, lignin, glycine, a Northumberland coal and a South Wales anthracite. It became obvious that more studies must be made before the mechanism of the catalysis of carbon combustion by admixtures of other than alkali salts can be elucidated. There seems to be little doubt that the main function of alkali carbonate is to break down stable surface oxides and so present a clean carbon surface to the oxidising gas. The mode of addition of the catalyst is of importance. The catalytic activity of potassium cyanide is more like that of the chloride than that of the carbonate, which suggests that the lattice structures as well as the chemical properties of the catalysts are involved.

Blast Furnace Gas Burning. F. X. Gilg. (Blast Furnace and Steel Plant, 1943, vol. 31, Feb., pp. 224-228). The author describes some recent designs of steam-generating plant fired by combinations of blast-furnace gas and coke-oven gas with oil or pulverised coal. The development of turbulent burners for blast-furnace gas has made possible the burning of this gas with no more excess air than that required for pulverised coal. Boilers are now in use with furnaces measuring less than 21 ft. from burner wall to water-cooled rear wall as compared with high furnace designs having a flame travel of 30-40 ft. from burner wall to boiler tubes.

Coke Oven Plant Construction and Development in 1942. W. A. Leech, jun. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 60-67). The author reviews the construction and improvements of coke-oven batteries in the United States in 1942. Increased productive capacity has been obtained by increasing the oven height; uniform heating of the higher ovens is provided by recirculation of waste gases from the down-flowing or "off-heat" flues by aspiration with the fuel gas jet into the combustion or "up-burning" flue. A plant with three low-differential saturators for manufacturing ammonium sulphate is briefly described. The saturators are built outside the plant buildings and have easily removable cracker pipes. Thin lead linings protected by special bricks are now used in cracker pipes instead of heavy lead linings.

Coke Ovens and War-Time Conditions. R. J. Barritt and C. H. Newby. (Year Book of the Coke-Oven Managers' Association, 1943, pp. 189-201). The authors discuss the difficulties arising in the operation of coke-ovens in war-time. These are of two kinds: (a) Damage to oven soles due to fusion or excessive wear, and spalling of oven walls; and (b) breakage of door-frames and damage to self-sealing doors, particularly on the discharge side. A coal containing, say, 15% of moisture very often shows no sign of dripping in the charging car, but within half an hour after charging the oven, water may be seen running from the base of the doors; the reason for this is that the viscosity of water near its boiling point is much less than that at the initial temperature of

the coal when charged. Where coal is fed rough to drainage bunkers and crushed on its way to the service bunker, there is little chance of drainage taking place in the oven. Damage arising from black-out conditions is discussed and recommendations on oven operation in short and long "alert" periods are made.

The Examination of Coal as a Guide to Coke Oven Projects. F. S. Townend and H. M. Spiers. (Year Book of the Coke-Oven Managers' Association, 1943, pp. 300-313). The authors describe laboratory and full-scale coking-coal tests which they recommend with a view to determining the probable behaviour and yield of coal-blends in coke-ovens. These tests fall into four types: (1) Analysis; (2) determination of coking and plastic properties; (3) assay for yield of coke and by-products; and (4) fusibility and composition of ash.

A Survey of German Low-Temperature Carbonisation Technique. (Coke and Smokeless-Fuel Age, 1943, vol. 5, Apr., pp. 68-72, 78; May, pp. 84-88). A survey is made of the low-temperature processes for carbonising brown coal and bituminous coal in Germany. Data are presented on the properties and characteristics of the coals used and of the coke, gas, tar and by-products produced.

Properties of Blast Furnace Cokes. H. H. Lowry and M. A. Mayers. (Iron and Steel Engineer, 1943, vol. 20, Feb., pp. 36-44). The authors discuss those factors relating to coke quality which they consider should receive more than the attention which is usually paid to them. Not only should the average size of the coke comply with the blast-furnace requirements, but the size range should also be within certain limits. Investigations by the Bureau of Mines indicate that for every 100° F. increase in the final coking temperature the average size decreases 0.5 in. and the size range decreases 0.1 in. The porosity of coke has been found to depend mainly on the moisture content of the coals charged and not on any other items in the proximate analysis. The literature on the value of test data for coke as criteria for its performance in the blast-furnace is reviewed.

Combined Primary and Secondary Blast Furnace Gas Washer. S. P. Kinney. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 113-116). The author describes a gas-washer for cleaning blast-furnace gas, which has now given two years' satisfactory service in the Pittsburgh district. The gas is taken directly from the dust-catcher, and it is cleaned from 8 grains to 0.014 grains of dust per cu. ft. at the rate of 18,000 cu. ft. per min. The cleaning is effected by a high-pressure spray of water which, together with the gas, passes through a venturi tube and impinges on a deflector plate equipped with double serrated edges; this mechanism is called the stationary disintegrator. The standard pattern disintegrator operates at 150 lb. per sq. in. pressure of water, and 11 gal. of water clean 1000 cu. ft. of gas. Several disintegrators are arranged in parallel in the washing tower.

PRODUCTION OF IRON

(Continued from pp. 36 A-37 A)

The Blast Furnace Skip Hoist. G. Fox. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 58-64). The author discusses electrically driven blast-furnace skip-hoists, showing how the torque requirements vary from the starting of a loaded skip to the tipping position at the top of the furnace, and methods of controlling hoists driven with two motors.

Résumé of Blast Furnace Practice in 1942. W. A. Steele. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 68-70). The author reviews blast-furnace construction and practice in the United States during 1942. Whereas in 1917 395 furnaces produced 43 million tons of pig iron, the production in 1941 was 56 million tons from 213 furnaces. Sintering plants have been enlarged and new ones built. The first all-welded furnace has been constructed and blown in. The installation of plant for removing moisture from the blast has proved to be of both technical and economic advantage in the South, but its economy in northern plants has not yet been proved.

Relationship of Pig Iron Production to the War Effort in 1942. W. A. Haven. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 102-103). The author describes how the production of pig iron in the United States was increased in 1942. The high production was achieved partly by the construction of new 1000-ton-per-day furnaces and partly by driving the existing furnaces harder. The author deprecates the construction of plants to make sponge iron from lean ores.

Smelting Sinter in the Blast Furnace. C. E. Agnew. (Steel, 1943, vol. 112, Feb. 15, pp. 100-104, 135-139; Feb. 22, pp. 88-97). In discussing the theory of the blast-furnace process the author explains the chemical, physical and thermal conditions governing the production of iron and what would be the characteristics of an ideal ore. The preparation of sinter and the extent to which it approaches an ideal ore are then considered. The factors governing the preferred particle size of sinter are the desire to transmit heat as rapidly as possible from gas to stock, and the desire for free passage of the gas through the interstices of the stock. To meet the former requirement fines are desirable because of the large ratio of surface to mass, and for the latter requirement larger sizes are needed. The ideal minimum is that particle size which will not easily be entrained in the ascending gas stream. A sinter graduated from 1 in. down to particles held by a 100-mesh screen, with as large a percentage of fines as possible consistent with the free flow of gas, is the ideal. The greater physical strength of sinter as compared with natural ore not only permits, but makes desirable,

a smaller particle size of coke than is usual with the soft ore operations. It must be recognised that if the soft ore to be sintered contains a proportion of gangue which causes the sinter to be of relatively large particle size with a deficiency of fines, some of the sinter must be crushed to get the fines. Iron silicates in the sinter are detrimental because they cover the iron oxide and impede its reduction. Beneficiated material eliminates the principal cause of irregularity in furnace operation by eliminating the restriction to gas flow through the stock column. The ideal condition would be to have uniform resistance to the gas flow over horizontal sections of the furnace, in which case the distribution of gas and heat would also be uniform.

Blast Furnace Metallurgy. C. D. Smith. (Eastern States Blast Furnace and Coke Oven Association : Steel, 1943, vol. 112, Mar. 29, pp. 86-92). The author reports on observations made in an attempt to correlate the production of iron for Bessemer converters to various factors influencing the blast-furnace process. The highest rate of production was obtained with a tapping temperature in the 2690-2750° F. range. In this optimum temperature range the silicon content was always between 1.15% and 1.40% and the sulphur between 0.035% and 0.055%. An increase in the blast volume from 45,000 to 56,000 cu. ft. per min. increased the production by 21%. It is best to maintain the highest possible volume of blast consistent with not too much flue dust. The highest production was obtained with 60-80 tons of scrap per day in the charge. The installation of a coal washer for the coking coal reduced the ash content of the coke from 9.67% to 8.86% and the average sulphur content from 1.03% to 0.962%, and the beneficial effect of this on the operation and production of the blast-furnace fully justified washing the coking coal.

Recent Improvements in Stopping Blast Furnace Tap-Holes. A. G. Arend. (Metallurgia, 1943, vol. 27, Apr., pp. 232-233). The author describes improved mechanism for the operation and control of piston-type clay guns for stopping blast-furnace tap-holes.

Developments in the Production of Hard Metals. H. Wolff. (Iron and Steel Institute, 1943, Translation Series, No. 148). An English translation is presented of a paper on the production of sintered carbide die and cutting tools; the original appeared in Teknisk Tidsskrift, 1941, vol. 71, Dec. 27, pp. 549-551 (see Journ. I. and S.I., 1943, No. I., p. 197 A).

FOUNDRY PRACTICE

(Continued from pp. 38 A-44 A)

Rationalisation in Iron Foundries. Part II. Application of Principles. F. L. Meyenberg. (Metallurgia, 1943, vol. 27, Jan.,

pp. 151-153; Mar., pp. 188-190; Apr., pp. 223-226). Continuing his series of articles (*see* Journ. I. and S.I., 1943, No. I., p. 152 A) the author deals in this part with the application of the principles of rationalisation to the particular case of iron foundries, discussing this in separate sections on studies of organisation, time and costing.

Unusual Foundry Design. (Iron and Steel, 1943, vol. 16, May, p. 324). A brief description is given of the iron foundry at the Burmeister and Wain shipbuilding yard at Copenhagen. It is housed in a circular building 282 ft. in dia. with an interior height of 72 ft. at the centre. The centre column carries one end of each of seven overhead electric travelling cranes; the four largest of these can pass over the three smaller ones. There are two cupolas melting 18-20 tons per hr. and a third melting 14-16 tons per hr.

The Effect of Ladle Additions on the Properties of Cast Iron. E. Piwowarsky. (Iron and Steel Institute, 1943, Translation No. 143). An English translation is presented of a paper which appeared in *Giesserei*, 1940, vol. 27, Jan. 26, pp. 21-30; Feb. 9, pp. 47-52 (*see* Journ. I. and S.I., 1940, No. I., p. 258 A).

Ladle Additions to Cast Iron. E. Piwowarsky. (Iron and Steel Institute, 1943, Translation No. 144). An English translation is presented of a paper which appeared in *Giesserei*, 1940, vol. 27, Apr. 5, pp. 124-125 (*see* Journ. I. and S.I., 1940, No. II., p. 9 A).

High Test Iron Production Is Not Difficult. A. P. Alexander. (Foundry, 1943, vol. 71, Mar., pp. 92-94, 181-185). The author gives information on cupola practice for producing high-strength iron. Simple methods of calculating the correct coke-bed height and the additional coke required to compensate for the taking-up of carbon by steel in the charge are given. Steel should be charged on the coke, pig iron next, then scrap; small scrap or pig should be charged in the centre and heavy pieces near the wall. When more than five charges of 70% steel mixes are melted oxidation may be encountered; a much larger amount of the inoculant ferro-silicon will be needed, as it is difficult to graphitise oxidised iron. The procedure for making wedge tests is described.

Maintains Production of Quality Castings. F. W. Shipley. (Foundry, 1943, vol. 71, Mar., pp. 96-97). The author gives brief particulars of the results achieved by the cupola practice at the grey iron foundry of the Caterpillar Tractor Co., Peoria, Illinois, where a high proportion of a wide variety of scrap is included in the charge.

Acid Open-Hearth Practice for Steel Castings. C. W. Briggs and G. S. Baldwin. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1104-1129). The authors review American acid open-hearth practice in steel foundries. There are about seventy furnaces with rated capacities of from 10 to 125 tons operated by the acid process. Details are given of:
(a) Construction of the bottom and the tap hole; (b) composition

of the charge and the charging procedure; (c) melting down, oxidation and refining; and (d) slag sampling and control.

Making Steel in the Basic Electric Furnace for Navy Castings. S. W. Brinson and F. B. Anderson. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1211-1219). The authors describe the electric furnaces and steel-melting practice at the Norfolk steel foundry of the United States Navy. The furnaces include a 500-lb. and a 1000-lb. Lectromelt, a 3-ton Greaves-Etchells and a Swindell furnace 12 ft. in dia. They are all basic lined, and the steel is made under two slags. The second slag, when making a 15,000-lb. heat, consists of 300 lb. of lime, 100 lb. of fluor spar and 90 lb. of cement; about 10 lb. of coke dust are added, if necessary, to build up the carbon. After this slag has been in the furnace for 3-5 min. it is sprinkled with 3 or 4 shovels of lime mixed with aluminium borings or turnings in the proportion of 3 parts of lime to 1 part of aluminium by volume. In 5-10 min., as soon as the slag starts to melt, a foamy white slag forms. Usually lime only is added after that. About 300 lb. are added if the slag thins down sufficiently, for an attempt is made to finish this second slag with 40 lb. of lime to every 1000 lb. of metal. If the silicon content of the steel is to be under 0.20%, 0.05% of aluminium is added in the furnace just before tapping. 1 lb. of 30-35% calcium silicide per ton of metal is added in the ladle when tapping.

Ford Triplexing Installation. W. A. Phair. (Iron Age, 1943, vol. 151, Mar. 11, pp. 63-65). The author gives a brief description of the plant and processes at a steel foundry of the Ford Motor Company, where the triplex process is operated on a large scale. The equipment includes four cupolas, four side-blown converters, eleven electric furnaces, sand bins, moulding machines, conveyor lines, sand reclaiming units and heat-treatment furnaces. Working three shifts, the plant has a capacity of 600 tons of steel castings in 24 hr. Two cupolas are in constant use, the other two acting as stand-by units. The iron is transferred to the converters in 6-ton ladles. The converters are acid lined and of $5\frac{1}{2}$ -ton capacity, and each is fitted with portable, auxiliary push-button controls for tilting and levelling. The actual blowing time is 17-18 min. No additions are made in the converter, but manganese or silicon alloys are added in the electric furnace. The electric furnaces are primarily holding and mixing units, and the metal is held in them about 2 hr. to bring it to the required analysis and tapping temperature of 3050° F.

Centrifugally Cast Steel. C. K. Donoho. (Iron Age, 1943, vol. 151, Apr. 1, pp. 52-58). The author describes the equipment and process used in the manufacture of centrifugal steel castings at the foundry of the American Cast Iron Pipe Company. With sand-lined moulds a general rule is to use a spinning speed which will give a centrifugal force about 75 times that of gravity. The number

of revolutions per minute to attain this force is approximately equal to 1675 divided by the square root of the casting radius (in inches). Numerous illustrations of the plant and types of castings, which include bogie-wheel hubs, hawse pipes and ship's propeller shafts, are presented.

A Foundry Investigation of Bond Clay Properties. A. S. Nichols, F. W. Hintze and F. L. Overstreet. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1257-1290). The authors report on an investigation of the properties and requirements of bonding clays for moulding purposes. A test procedure was devised in which moulding sands were prepared each containing one of the clays frequently used as a bond. The sands were held to uniform green strengths and contained sea coal in commonly-used proportions. A specially designed casting, which would be subject to a large number of defects generally attributed to sand, was used. The same moulding and casting technique was repeated each time. Ottawa silica sand was chosen as a base, and clays of illite, western montmorillonite, southern montmorillonite and kaolinite types were used. Tables and curves showing the results of many tests on the prepared sands are given. The general conclusions were: (1) There is little important difference in the quality of castings produced in sands bonded with the clays tested when the sand is controlled by proper additions and kept within the limits of the desired specifications; (2) when additions of new sand to the used sand are discontinued the quality of the castings deteriorates rapidly if the sand is bonded with montmorillonite-type clays; (3) the defects usually attributed to extremes of permeability, dry strength and flowability were not consistently found in castings made in sands having extreme properties as measured in this investigation; (4) moulding, gating and pouring practice are responsible for more defects than any deficiency in the properties of the clay; (5) considerable savings in clay, sea coal and new sand additions can be made by using an illite-bonded sand; (6) the mixing operation is an important cost factor; the mixing period in this investigation was longer than the time usually spent in foundries, yet only 78-80% of the total potential maximum strength was attained on the initial batch; (7) the highest green strength is attained with a montmorillonite clay bond; the next best is the illite-bonded sand; (8) the loss of green strength with use is, however, least with the kaolinite and highest with the montmorillonite-bonded sand; (9) the dry strength undergoes considerable changes with use when the sand is bonded with montmorillonite and there is least change in this property with illite-bonded sand; (10) illite-bonded sands have the highest flowability and kaolinite-bonded the lowest.

The Importance of the Swelling Properties of Clay Binders for Foundry Sands. K. Endell, H. Reiniger, H. Jensch and P. Seaki. (Iron and Steel Institute, 1943, Translation No. 145). An English

translation is presented of a paper which appeared originally in *Giesserei*, 1940, vol. 27, Nov. 29, pp. 465-475; Dec. 3, pp. 499-502 (see *Journ. I. and S.I.*, 1942, No. I., p. 87 A).

The Arrangement of Cores, Blow Holes and Vents for Blowing Purposes. R. F. Lincoln. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1134-1151). The author describes the construction and operation of core-blowing machines. The lay-out of core-box equipment is very important in the maintenance of high rates of production. Two small boxes, convenient to handle, and used alternately, will produce more cores in a given time than a single heavy box containing double the number of cores. In deciding the position in which a core can be blown to the best advantage attention must be paid to the following points: (1) It is always desirable to direct the air stream downwards towards the larger sand sections instead of relying on the venting arrangement to pull the sand up into the pockets; (2) when possible the air stream should be introduced through the print sections of the core; (3) the natural venting of the box at the parting line, or on open print surfaces, should be utilised to the greatest possible extent, so that the amount of additional venting is kept at a minimum; and (4) when two or more cores are placed in one gang-box they should be arranged so that each core has its own free venting system.

The Use of the Hot Strength Test as a Tool for Controlling Core Mixtures. F. B. Riggan. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1185-1193). The author describes tests with different core mixtures with the object of improving the core strength and the surface condition of the castings. Tests with a dilatometer revealed that weak cores with a hot strength of 3-5 lb. were suitable for small castings, and that when required the hot strength could be increased up to 20 lb. and even higher by adding finely ground iron oxide (Fe_2O_3). Iron oxide additions prevented burning-in on the inside of castings where sharp corners or abrupt changes of section occurred.

The Problems of Making Large Castings. A. Lebesch, W. A. Hambley and K. Geist. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1222-1236). The authors discuss problems arising in the design and manufacture of large iron castings. A detailed description is given of the preparation of the mould and cores, the pouring and cooling of a casting, such as a 42-ton frame for a crushing machine, in a pit 14 ft. deep.

Make Piston Rings for War Machines. P. Dwyer. (Foundry, 1943, vol. 71, Mar., pp. 88-91, 179). The author describes the foundry practice at the works of the Perfect Circle Co., New Castle, Indiana, where cast-iron piston rings from 1 in. to 9 in. in dia. are made.

PRODUCTION OF STEEL

(Continued from pp. 44 A-45 A)

Open Hearth Practice Undergoes Some Modifications in 1942. L. B. Lindemuth. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 74-75). No very unconventional changes in open-hearth design and operation have been introduced in the United States to obtain increased production. Modifications in roof construction have been made to save labour in roof repairs. More hot metal has to be charged to make up the deficiency in scrap. One company had desiliconised the hot metal by adding mill-scale to the stream while pouring it from the mixer into the open-hearth charging ladle.

Problems of Total Operation in Steelmaking. W. C. Marshall and F. G. Norris. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1571 : Metals Technology, 1943, vol. 10, Apr.). The authors consider two steelmaking problems which are related to the co-ordination of blast-furnace and open-hearth operations and, in this sense, they may be called "total operation in steelmaking." The first problem is that of working out a phosphorus balance for the whole process when basic open-hearth slag is charged in the blast-furnace. A simple method of doing this from the following data is explained : (a) The percentage of phosphorus in the iron ; (b) the weight of new phosphorus (from ore and coke) in the burden ; (c) the iron production ; and (d) the proportion of the total open-hearth slag that is used in the blast-furnace burden. The second problem is that of the relative influence of factors affecting the average daily production of steel at an integrated plant. This production is shown to be dependent on the number of open-hearth furnaces in operation, the weight of hot metal delivered to these furnaces, the percentage of hot metal in the open-hearth charge, and the quality of the scrap as expressed by the average weight per box. Tables are presented of coefficients expressing the relative importance of these factors.

The Effect of Light Scrap on Open Hearth Practice. E. H. Reyer. (Blast Furnace and Steel Plant, 1943, vol. 31, Feb., pp. 205-207). The author describes open-hearth practice at a steel-works with three 175-ton furnaces using charges with very high proportions of scrap. Light scrap charges seriously affect the life of the furnace lining, for its bulk deflects the flame against the back and front walls. Copper in the scrap is detrimental to the rolling quality of the steel if more than 0.20% is present. Tin is detrimental to the physical properties of the finished steel, the effect being more pronounced with increasing carbon. Embrittlement is caused by 0.020% of tin in steels with 0.75-0.90% of carbon. Additional manganese tends to offset the effect of tin.

New Kink in Repairing Open-Hearth Bottoms. J. D. Sawyer. (Steel, 1943, vol. 112, Mar. 8, pp. 116-118, 139). The author describes a novel method of repairing a basic open-hearth furnace bottom which was successfully employed at a steelworks on the Pacific Coast. A bad boil had occurred in front of No. 1 door in No. 3 furnace; the heat had to be tapped early, but the last few cwt. of slag went through the bottom and through the pan; nearly 8 tons of magnesite were used in the repair after the hole had been closed with broken chrome bricks. The patch was finished by using the charging machine and an old charging box to transfer molten slag from No. 1 furnace and to dump it on the repaired hole in No. 3 furnace. The application of liquid slag on a deep hole repaired with a considerable quantity of magnesite saves much time and makes a better repair than several additions of a few inches of magnesite mixed with ground slag. The safe thickness of magnesite preceding the slag application is not less than 5 in. and not more than 10 in.

Arc Furnace Steelmaking To-Day. N. F. Dufty. (Iron and Steel, 1943, vol. 16, May, p. 318). The author asserts that, whilst progress has been made in the design and construction of the electric arc furnaces, its controls and equipment, no progress at all has been made in Great Britain during the last twenty-five years in arc furnace steelmaking practice. He urges more investigation of American and Russian practice, examination of the possibilities of Bessemer-converter/arc-furnace duplexing, the use of modern top-charging equipment and the better classification of scrap for use in electric furnaces.

Calcium and Some of its Applications. L. Sanderson. (Metallurgia, 1943, vol. 27, Apr., pp. 245-246). After briefly surveying the properties of calcium and the forms in which it occurs in nature, the author discusses the metallurgical applications of the calcium-silicon, calcium-manganese-silicon and calcium-aluminium-silicon alloys. Calcium-silicon contains 28-35% of calcium and, when added to molten steel in amounts of 2 lb. or more per ton, it considerably improves its fluidity; it is employed in basic electric furnace practice to develop with maximum rapidity a highly fluid reducing slag. Calcium-aluminium-silicon contains 10-14%, 8-12% and 50-53% of these elements respectively; when added to steel the deoxidation products have a comparatively low fusion point, and quickly coalesce into large particles that rise swiftly in the molten steel. The third alloy contains calcium 16-20%, manganese 14-18% and silicon 55-60%; its use improves the transverse strength in forged and rolled steel, as well as the ductility of steel castings.

REHEATING FURNACES

Furnace Has All-Door Front Wall. L. S. Longenecker. (Blast Furnace and Steel Plant, 1943, vol. 31, Feb., pp. 220-222). The author describes a special design of reheating furnace with three doors in the front wall so constructed that the two buckstays separating the doors can also be lifted; there is thus no dead hearth space behind the buckstays which is inaccessible to the charging machine.

Experiences in the Construction and Operation of Modern Pusher-Type Furnaces. T. Stassinot. (Iron and Steel Institute, 1943, Translation Series, No. 131). An English translation is presented of a paper which appeared in *Stahl und Eisen*, 1939, vol. 59, Jan. 19, pp. 54-63 (*see* Journ. I. and S.I., 1939, No. I., p. 216 A).

FORGING, STAMPING AND DRAWING

(Continued from pp. 45 A-47 A)

Dimensions of Forging Die Blocks. P. Patek. (Heat Treating and Forging, 1943, vol. 29, Mar., pp. 129-131, 149). The author discusses the relation between the outside dimensions of die blocks and the size of the impression cut in them. Examples are given of the method of calculating the thickness of die walls for certain types of impression.

Improved Forging of Crankshafts. A. G. Arend. (Drop Forger, 1943, vol. 22, Feb., pp. 180-186). The author discusses the design of counterstroke, or double, hammers, in particular those for forging 6-throw and 4-throw crankshafts. In two recent counterstroke hammer designs, the upper tup is driven by an overhead cylinder in the general manner usually associated with earlier steam hammers, but the lower tup is propelled against the upper by means of a resilient connection actuated from the upper tup. With one of the latest models, the power is transferred to the lower tup through a bundle of 20 light steel bands on each side of the upper tup.

A Report on the Overheating of Steel Forgings. S. T. Melling. (Drop Forger, 1943, vol. 23, May, pp. 16-20). The author discusses methods adopted by aircraft engine manufacturers and their forging suppliers to detect overheating in steel forgings. The less severe stages of overheating are naturally the most difficult to detect. Fracturing integral test-pieces is the only generally adopted test for overheating. With small forgings or stampings, a small percentage of actual components is sometimes tested by fracturing, but not all forgers do this. The fracture test does not always

detect local overheating; various etching methods have been employed, but none has been put on a satisfactory production basis. Parts to be tested by fracture should be in a condition such that they may be broken with a minimum number of blows to avoid shearing and tearing. The inspector must be well experienced in the examination of fractures. Rigid temperature control and the avoidance of prolonged soaking and flame impingement are essential to prevent overheating in the forge furnace.

Defects in Steel for Drop Forgings. H. J. Merchant. (Drop Forger, 1942, vol. 22, Nov., pp. 117-123; 1943, Feb., pp. 161-166). The author discusses the following defects which can arise in steel billets and bars and how these affect subsequent drop-forging: pipe, axial segregation, other types of segregation, seams, shell, rokes, ganister, non-metallic inclusions, mill-scale, roll marks, incorrect size and mixed steel. Once the steel for a forging is made, its inherent grain size cannot be altered. The best time to check the inherent grain size is before the steel is forged, so that work need not be wasted on steel the grain size of which may be unsuitable for some high-duty application.

Practical Programs for Reclamation of Metal Scrap—Steps to Minimize Amount of Scrap Produced. J. L. Cannon. (Metal Progress, 1943, vol. 43, Apr., pp. 561-562). The author makes recommendations for reducing the amount of scrap produced in the pressing, stamping and machining of metals.

Recent Progress in Cold Drawing of Seamless Steel Tubes. D. W. Rudorff. (Iron and Steel, 1943, vol. 16, May, pp. 314-317). The author presents an abridged English translation of an investigation, reported by H. Frank, of the factors affecting the degree of reduction obtainable per pass in tube-drawing mills (*see* Journ. I. and S.I., 1943, No. I., p. 14 A).

Phosphatic Coatings as Aids in the Plastic Working (Cold Drawing) of Metals. A. Durer. (Zeitschrift des Vereines Deutscher Ingenieure, 1942, vol. 86, Jan. 10, pp. 15-18; Sheet Metal Industries, 1943, vol. 17, June, pp. 1025-1027). An abridged English translation is presented of a paper in which the beneficial effects of a phosphate coating in the cold-drawing of steel sheet is discussed. The coating has a higher capacity for oil-adsorption than the bare surface of pickled steel, and it is capable of plastic deformation, provided that it adheres firmly to the base metal. (*See* p. 28A.)

Relative Workability of Metals. A. G. H. Andersen. (Wire and Wire Products, 1943, vol. 18, Mar., pp. 161-167, 178-179). The author develops formulæ and curves to express the relationship between the force required to draw wire through a die and the degree of reduction; he shows how the force increases with successive drafts owing to the work-hardening of the material.

ROLLING-MILL PRACTICE

(Continued from pp. 16 A-17 A)

Electrical Developments in the Steel Industry during 1942. F. Mohler. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 76-80). The author describes briefly some developments which have taken place in the electrical equipment for steelworks in the United States in 1942. The first blooming mill equipped with amplidyne control has been placed in service; this system permits the use of relays carrying a fraction of an ampère instead of contactors carrying hundreds of ampères. For electric arc furnace control an amplidyne generator can be used to supply power directly to each electrode motor; because of its high sensitivity and rapid response, this control provides more accurate, faster and smoother operation of the electrodes. Rectifiers and methods of control for plate, strip, bar and tube mills are discussed.

Recent Developments in Steel Plant Electrification. A. F. Kenyon. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 88-92). The author gives some particulars of electrical equipment supplied in 1942 for new rolling-mill stands in American steelworks.

Recent Electrical Developments Aid Steel Production. A. F. Kenyon. (Industrial Heating, 1943, vol. 10, Jan., pp. 68-74). The author gives brief descriptions of the motors and electrical equipment which have recently been installed at some of the American rolling mills to meet the increased demand for ship plates and armour plate.

Standard Costs for Power Consumption in Rolling Mills. F. Ryder. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 104-108). The author explains methods of working out the power consumptions of rolling mills and discusses how the power requirements are affected by changes in the composition of the steel and the ratio of the roll diameter to the thickness of the material being rolled.

Time Control in Rolling Mills. A. E. Lendl. (Iron and Steel, 1943, vol. 16, Apr., pp. 278-282, 296). The author discusses factors affecting stoppages in rolling mills and the use of mill time recorders to ascertain the cause of lost time and methods of improving efficiency. Some examples are given which relate to the rolling of strip.

Rolling Pressures in Strip Mills. M. D. Stone and J. I. Greenberger. (Iron and Steel Engineer, 1943, vol. 20, Feb., pp. 61-69, 72). The authors develop equations for calculating the pressure on roll necks in the cold-rolling of strip and explain how the following factors influence this pressure: (a) The properties of the material being rolled; (b) the temperature of the material; (c) the speed of deformation; (d) the value of the ratio $\mu L/T$, where μ is the

coefficient of friction; L the contact length and T the initial thickness of the material; and (e) the tension on the strip.

Roll Oils and Coolants for the Cold Mill. M. Reswick. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 73-78). The author discusses the requirements of oils suitable for the lubrication and cooling of roll surfaces and strip in cold-rolling mills. The characteristics of five types of oil are considered, namely, straight mineral oils, mineral oils compounded with animal and vegetable fats, soluble oil and water emulsions, soluble oil and palm-oil emulsions, and straight palm oil. A plant for reconditioning palm oil is described, and reference is made to the use of emulsifiable fats or proprietary chemical compounds to replace palm oil.

The Evolution of the Modern Rail. (British Steelmaker, 1943, vol. 9, June, pp. 255-257). A brief account of the evolution of the steel rail from the laying of the first Bessemer steel rails in 1862 is given. Since 1931 the London and North-Eastern Railway Co. has standardised a quality of rail containing manganese 0.90-1.10% and carbon 0.50-0.60% for their entire system with the exception of positions subject to exceptionally heavy wear, such as the crossings at Newcastle and York, where the additional cost of 12-14% manganese steel is justified.

Improving Production in the Shearing of Circular Plates with Rotary Shears with the Aid of Work- and Time-Studies. E. Kratschmar. (Archiv für das Eisenhüttenwesen, 1943, vol. 15, June, pp. 559-561). The author describes how time studies were carried out on the operation of cutting circular steel plates 620 and 930 mm. in dia. with the object of increasing production and arriving at an equitable wages agreement.

Modern Cold Sawing Technique. N. A. Malone. (Iron and Steel Engineer, 1943, vol. 20, Feb., pp. 29-34). The author describes a very recent design of circular saw for cold-sawing steel in which the downward feed and all movements of the saw carriage are performed hydraulically, whilst the saw itself is rotated by an electric motor. A curved gullet form of tooth was developed which improved the performance of cold-sawing machines by about 30%. The blade has "lead" and "follow" teeth positioned alternately. The lead teeth are higher and narrower and cut a centre groove, and the follow teeth are wider and cut two narrow chips from the sides of the centre groove. The relationships between rate of feed, peripheral velocity and hardness of the steel being cut are discussed.

HEAT TREATMENT

(Continued from pp. 47 A-49 A)

Some Notes on Armor Plate for Ships and Tanks. (Metal Progress, 1943, vol. 43, Mar., pp. 383-387; Iron and Coal Trades

Review, 1943, vol. 146, June 18, pp. 923-925). After a brief account of the history of the development of armour plate, some details are given of modern methods of producing Krupp cemented armour plate, termed "Class A" armour by the American Navy, of the ballistic tests to which it is subjected, of lighter and more ductile armour and of the methods used to support armour plate on ships.

Case-Hardening and Gear Manufacture. D. McPherson. (Machine Shop Magazine, 1943, vol. 4, May, pp. 65-69). The author makes a critical survey of existing case-hardening practice. It is not generally realised what an important item the case-hardening process is in the total cost of a finished part. It is not uncommon to find that a simple roller shaft costs 4*d.* to machine and, depending on its size, 2*s.* to 5*s.* to case-harden. Case-hardening as generally practised produces a hard surface of varying depth, the structural characteristics of which depend upon such a number of variables as to make reproducibility impossible except under the most rigorous technical supervision. Given the rigorous supervision, the reproducible structures obtained, by virtue of their heterogeneity and extraordinary variation of refinement in addition to the internal stresses resultant and dependent upon heat treatment, are theoretically most unsuitable for arduous wear-resisting service.

Flame Hardening Tank Turret Ring Races. T. E. Lloyd. (Iron Age, 1943, vol. 151, Mar. 25, pp. 64-65). The author gives some details of the flame-hardening equipment and method of operation for hardening the surfaces of tank-turret ring races. A circular jig was devised to which the ring is clamped. The jig revolves at a controlled speed carrying the ring past the burner head and quenching jet, and immersing the ring in a tank underneath the workbench, where the temperature is rapidly stabilised without distortion.

Furnaces for Stress Relieving Armament Components. Section XII. (Industrial Heating, 1943, vol. 10, Jan., pp. 15-24; Feb., pp. 167-178). Descriptions are given of several types of car-bottom and pit stress-relieving furnaces for welded gun-turrets, iron and steel castings, and welded assemblies used in armament manufacture. Numerous illustrations and diagrams are presented.

Electric Furnaces in War Production. C. L. Ipsen. (Industrial Heating, 1943, vol. 10, Jan., pp. 28-32). The author describes and illustrates some electric furnaces for heat-treating steel cartridge cases, annealing stampings and hardening gears.

Checking Points and Suggestions for Keeping Industrial Furnaces in Condition. J. Wallerius. (Industrial Heating, 1943, vol. 10, Feb., pp. 190-196). The author makes recommendations for the maintenance of burners, piping, blowers and refractories for oil- and gas-fired industrial furnaces.

Network of Shops for Heat Treating Small Armor. L. Stouffer. (Metal Progress, 1943, vol. 43, Mar., pp. 390-391). The author gives an account of the way in which a number of formerly com-

petitive manufacturers of automobile springs, ironmongery, stampings, furnaces, saws, shovels and railway equipment in the Detroit district were organised for the combined production of heat-treated armour plate for tanks.

Some Notes on the Processing of Armor-Piercing and Semi-Armor-Piercing Small Caliber Shot. C. A. Litzler. (Industrial Heating, 1943, vol. 10, Mar., pp. 327-334). The author describes some of the methods by which armour-piercing shells of 3 in. dia. and less are heat-treated, cleaned, tested and ground. In mass production, high-frequency induction hardening is often employed, the operation taking $2\frac{3}{4}$ min. Of this time, the current is flowing for $1\frac{1}{2}$ min., then, after a 15-sec. interval, a cold-water quench is applied for about 1 min. The shell base is tempered to a lower hardness than the nose, and this can be done in 3 min. In order to detect excessive residual stresses in the shell bodies they are subjected to thermal shock by immersion first in ice-cold water, then in boiling water and finally in ice-cold water; this drastic treatment develops cracks in an over-stressed shell, and these are subsequently revealed by the magnetic powder process.

Hardening from Rolling Heat. D. W. Rudorff. (Iron and Steel, 1943, vol. 16, Apr., pp. 309-312; May, pp. 343-344). The author presents an abridged English translation of a recent paper by R. Schäfer and W. Drechsler on an investigation which proved it was economically possible to harden rolled alloyed and unalloyed steels direct from the heat of rolling. (See Journ. I. and S.I., 1943, No. I., p. 56 A).

Calculation of Jominy End-Quench Curve from Analysis. J. Field. (Metal Progress, 1943, vol. 43, Mar., pp. 402-408). It is sometimes desirable to have Jominy end-quench hardenability data for a steel of given analysis and grain size when the steel itself is not available for test. In the present paper the author proposes a method of constructing the Jominy hardenability curve which is based on the following assumptions: (1) The hardness at the quenched end of the Jominy specimen is a function of the carbon content; (2) the hardness at any distance from the quenched end is a function of the carbon content, the amount of alloying element and the grain size; and (3) the ratio of the hardness at the quenched end to that at any distance from that end is a function of the ideal critical diameter as determined by M. A. Grossmann (see Journ. I. and S.I., 1942, No. II., p. 219 A). The proposed method has been checked by tests from 43 different heats of various grades of steel, and in the majority of cases the calculated values were in good agreement with the actual test results.

Quench Control Pays by Assuring Better and More Uniform Hardening. R. Trautschold. (Steel, 1943, vol. 112, Mar. 1, pp. 106-108). The author describes the oil-quenching equipment at the works of the Ross Gear & Tool Co., in Indiana. One tank 45 ft. long containing 6000 gal. of oil is used to quench batches of

parts which are discharged from six horizontal-retort carburising furnaces. A linked conveyor with a central horizontal section 24 ft. long in the bottom of the tank passes into and out of the oil. The load (about 500 lb.) from each furnace slides down a short inclined chute to a vertical chute, through which it drops on to the horizontal section of the conveyor. The conveyor is electrically driven, and its speed can be controlled between 3 and 12 ft. per min.

WELDING AND CUTTING

(Continued from pp. 50 A-53 A)

Chain Welding by Semi-Automatic and Automatic Methods. (Machinery, 1943, vol. 62, June 10, pp. 626-629). Processes of making heavy ship's chains by fire-welding and electric butt and flash welding are described and illustrated.

Tests on NE 8630 Steels for Welded Air Frames. M. Hill. (Metal Progress, 1943, vol. 43, Apr., pp. 555-559). The author reports the results of weldability tests carried out by the United States Air Forces on the low-alloy National Emergency steel 8630 which is used for tubular frames for aircraft.

Weldability of High Tensile Structural Steels. W. G. John. (Welding, 1943, vol. 11, June, pp. 274-278). The author makes recommendations on the technique for welding high-tensile steel, especially in the construction of ships.

Arc Welding Tool Steel with Stainless Electrodes. H. W. Rushmer. (Iron Age, 1943, vol. 151, Mar. 11, pp. 51-55; Machine Shop Magazine, 1943, vol. 4, May, pp. 48-52). The author describes some examples of the successful welding of high-speed steel to carbon steel by preheating the parts and welding with stainless steel electrodes. The examples include lathe tools, lathe centres, screw-threading taps and gauges.

Nicking and Breaking Billets into Shell Blanks. G. V. Stottman and R. F. Helmkamp. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 65-71). The authors describe various nicking and breaking practices as carried out at different steelworks for cutting billets into the lengths required for shell forgings. Both manual and machine oxy-acetylene cutting are employed for cutting the nicks. Data on oxygen consumption and cutting speeds are presented and several types of equipment are illustrated.

Flame Cutting. (Ministry of Supply: Automobile Engineer, 1943, vol. 33, May, pp. 211-213). A summary is presented of the information given in two bulletins prepared by the Department of Tank Design, Ministry of Supply, for the guidance of those engaged in the preparation and profiling of rolled armour plates for fighting vehicles. Data are presented on the optimum gas pressures, cutting

speeds, depth of heat-affected zone when cutting high-alloy steel plate from 5 to 100 mm. in thickness with the oxy-acetylene, oxy-propane or oxygen/coal-gas flame.

MACHINING

Machinability of National Emergency Alloy Steels. O. W. Boston. (Metal Progress, 1943, vol. 43, Apr., pp. 543-547). The author reviews the experiences reported by a number of engineering firms on the machinability of the National Emergency steels. On the whole they have proved to be just as machinable as the steels which they replace. Some adjustment of tool angles, cutting speeds and feed rates has been necessary to establish the best cutting conditions.

Recent Developments in Carbides Vs. High-Speed Steel. H. A. Oldenkamp and J. McFadyen. (Mechanical Engineering, 1943, vol. 65, Apr., pp. 253-256). The authors make recommendations on the use of carbide tools for a variety of machining operations. The grinding and setting-up of carbide tools is so different from that of high-speed-steel cutters that the ordinary operator cannot do this without special training; a centralised tool-control system has been found essential. The grinding of carbide tools should be done by hand whenever possible, because the amount of heat at the tip can then be controlled more readily. A carbide tool wears more quickly, operating at too slow a speed, than when the work is turned too fast.

Cemented Carbides. (Automobile Engineer, 1943, vol. 33, Apr., pp. 161-164). A review is presented of the development of cemented carbide cutting tools in which information is given on tool angles, grinding wheels and technique for sharpening carbide tools, general and some specific applications, and machining speeds and feeds.

New Slants on Carbide Tools. G. G. Thompson. (Iron Age, 1943, vol. 151, Mar. 25, pp. 59-63). The author makes recommendations on the design of tungsten-carbide-tipped cutting tools, pointing out their limitations and giving examples of good and bad design for the same machining operation.

Have You Recently Appraised the Cutting Fluids? J. Geschelin. (Metal Progress, 1943, vol. 43, Apr., pp. 548-549). The author advocates that more attention be given to the selection of cutting fluids in machine shops, especially when new steels are being machined. Both the steel and the machining operation form criteria to the type of liquid to be used, and, when this has been decided, a short shop test can be carried out on the basis of which the final selection is made.

Practical Programs for Reclamation of Metal Scrap.—Disposal of Recoveries. H. J. Beattie. (Metal Progress, 1943, vol. 43, Apr., pp. 568–569). The author explains the guiding principles adopted by the General Electric Company for the disposal of turnings and borings, or “recoveries,” which are collected at their works. At the large manufacturing plants most of the scrap is classified and sold in a condition ready for use by the consumers, and the material is ready for despatch within 24 hr. of collection. About 20% of the scrap is re-used as raw material in their own works. Steel scrap is prepared for charging in electric furnaces for making steel castings. Cast iron is broken up and charged in the cupolas.

Practical Programs for Reclamation of Metal Scrap—Modern Chip Handling. A. M. Perrin. (Metal Progress, 1943, vol. 43, Apr., pp. 566–569). The author describes the equipment and layout for the conveying, cleaning, crushing and briquetting of cast-iron borings and steel turnings. Steel turnings are fed manually into the crusher; if they have been machined with mineral cutting oil, the chips are conveyed to a storage hopper serving the oil-extracting equipment. After removal of the oil, they are transported through another pneumatic conveyor to the proper compartment in the bins serving the briquetting press. Steel turnings machined with soluble oil are conveyed directly from the crusher to another storage hopper above the briquetting press. The finished briquettes are stored in the foundry yard. This plant requires three men and deals with 6 tons of turnings and borings per hr. The pneumatic conveyor system has proved to be very satisfactory.

Practical Programs for Reclamation of Metal Scrap—Salvage in a Large Industry. F. D. Kent. (Metal Progress, 1943, vol. 43, Apr., pp. 564–566). The author gives a brief account of the salvage organisation at the plant of the Wright Aeronautical Corporation. The collection and segregation of different scrap metals have been in force at these works for many years before the present war. All departments co-operate, and the need for salvage collection is made clear to new employees by the employment department. The propaganda for collecting scrap is maintained constantly without resort to spasmodic drives. All machine tools working on a single type of metal are lettered with a V in a colour which is distinctive for that metal throughout the works, and all collecting trays, barrows and bins for that metal are also marked in the same colour.

Practical Programs for Reclamation of Metal Scrap—Program for a Medium Sized Plant. E. S. Hoopes, jun. (Metal Progress, 1943, vol. 43, Apr., pp. 562–564). The author makes proposals for the establishment of a scrap-recovery organisation in a machine shop where finished parts of different alloy steels are made. The steps which a salvage manager should take are: (1) Train employees to know the types and nature of the scrap; (2) develop

an organisation capable of collecting and transporting the scrap; (3) obtain equipment for handling and preparing the collected scrap; (4) provide adequate storage facilities; (5) acquaint the plant personnel with the need for salvage and its economic aspect; and (6) establish a system of reporting the quantities of scrap collected and sold.

PROPERTIES AND TESTS

(Continued from pp. 53 A-56 A)

The Significance of Tensile and Other Mechanical Test Properties of Metals. H. O'Neill. (Institution of Mechanical Engineers, June, 1943, Preprint). Critical consideration of the conventional quantities obtained from the tensile test reveals their limitations for design purposes, especially where notch-fatigue effects predominate. Against such notch-fatigue the importance of high work-hardening capacity in a metal is emphasised, and its relation to tensile elongation behaviour outlined. It is suggested that even conventional tensile records may yield some rough measure of work-hardening capacity prior to cracking by means of quantities which, in this paper, are called "plasticity ratio" and "plasticity value." Attention is drawn to certain refined methods of plotting tensile diagrams. A review of published results indicates a basic generalisation for plastic deformation. If a graph of true stress P against one of the several forms of true strain ϵ be obtained, then the basic deformation diagram is, in general, the same for tension, compression, torsion and indentation. It consists first of a curved portion extending up to the point of critical plasticity which corresponds with the onset of necking in tension. The curve afterwards flattens out and continues upwards almost as a straight line. The complete diagram may be considered very approximately as of the logarithmic form $P = k\epsilon^m$, and its gradient (or the value of m) will be high in materials with very high strain-hardening capacity, and low in those which have been cold-worked.

Since work-hardening capacity has hitherto been largely determined by ball indentation tests, a correlation has been made between these and tensile tests. This has revealed some shortcomings of the Meyer n value for indentation. Heat treatment and plastic grain size influence the plastic properties of a metal and the effects of both have been studied. For specimens of various crystal sizes there is similarity in form between certain tensile and indentation diagrams. From these an appropriate ultimate true stress value may be obtained which is independent of the initial amount of cold work. Values for this pressure have been determined. The pressure of fluidity obtained by linear extrapolation

of a Stead true tensile stress-strain diagram is lower than that determined by heavy cold-rolling experiments. The deformation and strain-hardening which take place up to the point of "critical plasticity" (necking in the tensile test) appear to differ in internal crystallographic mechanism from that developing beyond this point. It is found that several physical properties reach limiting values at the necking stress.

Investigation shows that heat-treated steels with sorbitic microstructures may have a relatively low capacity for strain-hardening. Their employment under conditions of notch-fatigue is therefore not attractive. On the other hand, their resistance to wear may be relatively good. Wear remains a complex problem, but examples are given where relatively good wear resistance has corresponded with relatively high "plasticity values."

Some Tensile Shock Properties of Carbon Steels. F. V. Warnock and J. B. Brennan. (Iron and Steel Institute, 1943, this Journal, Section I). Previous work carried out by Smith and Warnock (*see* Journ. I. and S.I., 1927, No. II., p. 323) on the tensile shock properties of Lowmoor iron formed the basis of a similar investigation embracing a family of carbon steels and carried out on the same testing machine. The residual energy after fracture was accurately measured by a device designed for that purpose.

The results of static, single-shock and multi-shock tests are compared and show that both the single-shock energy and the ratio of the static energy to the single-shock energy are dependent on the carbon content. The elongation produced by single-shock tests differs in many cases from that obtained by static methods, but the reduction of area remains substantially unaffected by the method of testing. A limiting range of shock energy, dependent on the carbon content, was indicated. Maximum values of elongation and reduction of area were observed in the multi-shock tests. An increase in the number of shocks for rupture caused a rapid diminution in the values of these quantities.

Plastic Deformation of Metals. R. Saxton. (Metallurgia, 1943, vol. 27, Apr., p. 246). The author discusses recent research on the plastic flow of metals. One of the most successful methods of ensuring a high total percentage reduction and an even flow under pressure during the drawing of austenitic stainless steels is to coat them with lead. With steels, a greater reduction per draft produces higher tensile strength than a greater number of drafts producing the same aggregate reduction.

Fatigue of Steels as Influenced by Design and Internal Stresses. J. O. Almen. (American Society for Metals: Steel, 1943, vol. 112, Mar. 8, pp. 88-89, 132-136; Apr. 5, pp. 112, 146-149). The author discusses the causes of fatigue failures. From the standpoint of fatigue strength, more harm than good often results from the grinding of machined parts. The depth to which a metal is "injured" by machining is deeper than is generally believed. A

piece of steel rough-machined on a shaper was carburised for 8 hr. at 1700° F., cooled in the box, reheated to 1500° F., quenched in oil and tempered at 300° F. for 1 hr.; the machined surface was ground at right angles to the shaper marks to a depth 0.0055 in. below the last visible mark; it was polished and finally shot-blasted, whereupon both the machining marks and the grinding marks reappeared, showing that the material was not uniform in its resistance to the shot-blasting. The difficulties in the evaluation of residual stresses and the limitations to the value of laboratory-prepared fatigue-test specimens are pointed out.

Hardness Testing of High Speed Steel at High Temperatures. E. C. Bishop and M. Cohen. (Metal Progress, 1943, vol. 43, Mar., pp. 413-416, 442). The authors describe a Rockwell hardness testing instrument incorporating an electric furnace, with which hot hardness determinations of high-speed steel can be made. The Rockwell machine carries an extended diamond holder of high-speed steel with its own heating coil which is enclosed in the furnace muffle surrounded by a second heating coil. The muffle and base are of stainless steel and an anvil to hold the specimen rests on the latter. Three tubes are welded to the muffle, one for observation, one for illumination and the third carries the leads to two thermocouples and also acts as a nitrogen inlet. All the tubes are water-cooled. Up to 50 separate determinations can be made on a single specimen without removing it from the furnace. The temperature can be controlled within $\pm 2^\circ$ F. The diamond and its mounting have not been affected by temperatures up to 1100° F. Tests on 18/4/1 (tungsten-chromium-vanadium) steel and 6/6/4/2 (tungsten-molybdenum-chromium-vanadium) steel indicated that molybdenum is an effective substitute for tungsten as far as hardness at up to 1100° F. is concerned. Specimens of hardened 18/4/1 steel were tempered for different times at 1050° F. and cooled to room temperature for cold-hardness readings; they were then heated quickly to 1000° F. for hot-hardness testing. This revealed that maximum room-temperature hardness is attained by tempering for less than 1 hr., but tempering for 2½ hr. is necessary to produce maximum hardening as measured at 1000° F. A tempering-time/hardness graph reveals that complete decomposition of the retained austenite coincides with maximum hot-hardness, but occurs later than maximum cold-hardness. The decomposition of retained austenite on cooling 18/4/1 steel from 950° F. causes the room-temperature hardness to increase by one unit (Rockwell C scale), but the improvement is two units when the comparison is made at 1050° F.

Report of Steel Division Committee on Magnetic Powder Testing. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1242-1253). The Steel Division Committee on Magnetic Powder Testing appointed by the American Foundrymen's Association in October, 1941, was to present a report in the form of

a summary of the available information on this form of testing. The present report is regarded as introductory and it contains definitions of the terms used, an elementary study of lines of force and a brief explanation of the principles applied when detecting cracks in steel by the magnetic powder method.

The Development of Permanent Magnets for Electrical Measuring Instruments. H. Bumann. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 547-549). The author explains how to make calculations connected with the design of permanent magnets for electrical instruments of the rotating-coil type. Data due to W. Zumbusch are presented giving the analyses and magnetic properties of 11 permanent-magnet alloy steels.

The Physical Testing of Power Plant Materials. F. Alton. (Engineering and Boiler House Review, 1943, vol. 57, May, pp. 122-127). The author defines some of the terms used in tensile, creep and fatigue testing, and describes machines for testing metals used in the construction of boilers and turbines. Reference is made to a high-speed fatigue testing machine with which tests at any speed up to 10,000 r.p.m. can be made; this machine embodies an A.C. motor run by a frequency changer and the speed of the motor driving the latter need only be changed within the range of 500-2000 r.p.m. to attain a speed variation from zero to 10,000 r.p.m. of the motor driving the fatigue machine.

Sources of Hydrogen in Steel and Means for Its Elimination. C. A. Zapffe. (Metal Progress, 1943, vol. 43, Mar., pp. 397-401). The author gives evidence in support of the theory that hydrogen in steel causes defects in welds and in enamel coatings, pointing out possible sources of hydrogen and methods of eliminating the trouble. Three iron castings were fired with vitreous enamel; one had been treated with nitrogen and showed no blistering whatever; one had had extra scrap added to the melt and it developed marked blistering; the third had been treated with hydrogen and the enamel was very badly defaced indeed. The formation of only 1 oz. of iron rust from water liberates about 1000 cu. in. of hydrogen at N.T.P., which is sufficient to embrittle 500 lb. of steel. It is thought that only part of the hydrogen in the steel is responsible for embrittlement and other defects and that there is therefore a certain critical hydrogen pressure necessary to cause defects. In electroplating, substitution of anodic cleaning for pickling or cathodic cleaning helps to eliminate hydrogen. In enamelling, baking the slip to remove some of the water and controlling the hydrogen-bearing constituent of the furnace atmosphere is beneficial. A maximum annealing temperature of 1110° F. is advisable for removing hydrogen from weld metal.

Alloy Economies in Steel Production. W. D. Wilkinson. (Blast Furnace and Steel Plant, 1943, vol. 31, Jan., pp. 71-73). The author briefly describes some of the steps taken in the United States to conserve chromium and nickel in the manufacture of

alloy steels; the effect of boron in increasing hardenability is discussed. The properties of 16%-manganese steel are compared with those of 18/8 and 17/7 chromium-nickel steels.

Special Alloy Addition Agents. (Steel, 1943, vol. 112, Mar. 8, pp. 94-95, 117-120). End-quench hardenability curves and tables of mechanical properties are presented which indicate the improvement imparted to a number of high-manganese steels by ladle additions of special alloys containing two or more of the following elements: aluminium, boron, calcium, manganese, silicon, titanium and zirconium. All these elements are available in the United States and by using one of these addition agents the desired properties can frequently be obtained without resort to those alloying elements which are in short supply.

Effect of Boron Containing Additions on NE Steel. A. S. Jamieson. (Iron Age, 1943, vol. 151, Mar. 25, pp. 45-50). The author reports the results of tests to determine the effect of treating heats of National Emergency steels 9420 and 9440 with 36 lb. per ton of an addition agent containing titanium 20.0%, aluminium 13.0%, manganese 8.0%, zirconium 4.0% and boron 0.5%. The two steels are low-alloy nickel-chromium-molybdenum steels, N.E. 9420 containing carbon 0.23% and N.E. 9440 containing carbon 0.44%. The important effect was to increase hardenability, the effect being less on N.E. 9420 than on N.E. 9440.

User Report No. 11 on Experience with NE (National Emergency) Alloy Steels. (Steel, 1943, vol. 112, Mar. 8, pp. 96-102, 136, 145). Data and curves are presented showing the hardenability and mechanical properties of medium-carbon National Emergency steels alloyed with: (a) Manganese 1.60-1.90%; (b) manganese and molybdenum; (c) nickel, chromium and molybdenum; (d) manganese, silicon, chromium, nickel and molybdenum; and (e) manganese, silicon and chromium.

User Report No. 12 on Experience with NE (National Emergency) Alloy Steels. J. Sorenson. (Steel, 1943, vol. 112, Mar. 29, pp. 72-73). The author presents data which show that cast manganese-molybdenum National Emergency steels 8739 and 8744 have satisfactory properties for medium stressed motor lorry parts and are satisfactory substitutes for some of the S.A.E. low-alloy nickel-chromium steels.

How to Use the NE (National Emergency) Alloy Steels. (National Emergency Steels: Steel, 1943, vol. 112, Mar. 15, pp. 78-84, 91). Particulars are given of precautions to be taken in carrying out the Jominy end-quench test on specimens of the National Emergency alloy steels.

Hardenability in Evaluating Physical Properties of N.E. (National Emergency) Alloy Steels. C. Nilson and A. W. Herbenar. (Automotive Council for War Production: Steel, 1943, vol. 112, Apr. 5, pp. 118, 150-155). The authors discuss within what limits end-quench hardenability data can be used to predict the mechanical

properties of steel and the evaluation of the National Emergency steels by this test.

Ryerson Data on NE Steels. (Steel, 1943, vol. 112, Apr. 5, p. 116). A comprehensive table is presented of the tensile strength, yield point, elongation, reduction of area and Brinell hardness of a number of the 8000 and 9000 series of National Emergency steels after various forms of heat treatment.

Comparison Data Showing Relationship between Standard Steels and NE (National Emergency) Alloy Steels. (Steel, 1943, vol. 112, Feb. 22, pp. 102-105). A table and several series of curves are presented which enable comparisons to be made between the properties of the 8000 series of National Emergency steels and those of the standard steels they are intended to replace.

Specifications Issued for NE (National Emergency) Carbon Steels. (Steel, 1943, vol. 112, Mar. 8, pp. 90-98). Tables and graphs are presented showing the physical properties of National Emergency steels containing different amounts of manganese, the object being to indicate how reducing the manganese affects the strength and to promote the use of steels containing less manganese.

Brief Up-to-Date Picture of Development of NE (National Emergency) Alloy Steels. R. W. Roush. (Society of Automotive Engineers : Steel, 1943, vol. 112, Mar. 1, pp. 94-98, 135-137; Mar. 8, pp. 109-110, 137-139). The author reviews the development and properties of the National Emergency steels.

Development of Austenitic Manganese-Alloyed Steels for Aero-Engine Exhaust Valves. D. W. Rudorff. (Metallurgia, 1943, vol. 27, Apr., pp. 205-209). An account is given of an investigation, reported by H. Cornelius in Luftfahrtforschung, 1942, vol. 19, No. 2, p. 44, of German research on the relative merits of austenitic chromium-manganese-nickel steels and austenitic chromium-nickel steels for aero-engine exhaust valves. A 15/13/2 chromium-nickel-tungsten steel with 0.74% of manganese was taken as a basis and its properties were compared with those of 14 other chromium-nickel steels containing up to 8.86% of manganese. Tensile, impact, hardness, wear-resistance, scaling, nitriding and creep tests were carried out. No relationship between either hardness or grain size and wear resistance could be established. While the steels high in manganese exhibited slightly greater wear than the others, these wear tests are not regarded as conclusive. Six methods of nitriding were tested, and the difficulties encountered in the nitriding of high-manganese alloy steels were overcome by the cadmium-phosphate treatment described by B. Jones (*see* Journ. I. and S.I., 1937, No. II., p. 171 P). The thickness of the nitrided layer decreased with increasing nickel content; the carbon content had little effect on this thickness. Once the conditions for the successful diffusion of nitrogen into the material have been established, the inhibiting effect of manganese is less than that of nickel. The partial replacement of nickel by manganese had no adverse influence upon the

scaling properties of the steels tested. The divergence of the hardness values of all the steels at room temperature decreased considerably with increasing temperature in tests at up to 900° C. Tungsten can safely be replaced by vanadium without impairing the creep strength, but the vanadium content should not be more than 0.5–0.6% because of its adverse effect on the scaling. The general conclusion was that a material containing carbon 0.42–0.52%, silicon 1.5–2.0%, manganese 3.0–5.0%, nickel 6.0–4.5%, chromium 17.5–18.5% and tungsten 0.9–1.3% should prove a very satisfactory valve steel.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 56 A–57 A)

X-Ray Measurements of the Thickness of the Cold-Worked Surface Layer Resulting from Metallographic Polishing. H. C. Vacher. (Journal of Research of the National Bureau of Standards, 1942, vol. 29, Aug., pp. 177–181). A series of annealed specimens, each having a surface free from cold-work, was prepared from steel (carbon 0.34%), copper and aluminium. The surfaces were finished with one of several abrasives commonly used in preparing a surface for metallographic examination, and X-ray back-reflection patterns were obtained by using copper, cobalt and chromium targets. The thicknesses of the layers altered by the different abrasives were then determined. The results showed that back-reflection patterns can be used to estimate the thickness of cold-worked layers between 2 and 25 microns on annealed steel, between 2 and 42 microns on annealed copper, and between 5 and 95 microns on annealed aluminium.

Cast Iron Strength vs. Structure. R. R. Adams. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1063–1097). The author endeavours to find a correlation between the structure and the strength of cast iron. The author's method of classifying the structure requires data on the following characteristics: (1) The cell size which is found by comparison, at 25 diameters, with a standard chart showing seven different sizes; (2) the type of graphite at the edges and at the centre of the cells; and (3) the size of the graphite at the edges and centre of the cells. Tables are presented giving these characteristics for specimens of 176 different cast irons together with the tensile and transverse strengths. There was good correlation between the structure and the tensile strength, but no correlation between either the transverse strength or the Brinell hardness and the structure.

Note on Some Precipitation Effects Observed in Mild-Steel and Wrought-Iron Pipe. T. H. Schofield. (Iron and Steel Institute, 1943, this Journal, Section I). A microscopical examination of

a corroded mild steel hot-water pipe which had been in service for three years revealed the presence of a precipitate within the grains, the amount of which varied in individual grains and sometimes seemed to bear some relation to the crystallographic planes. Much of the precipitate was very fine, but some was in the form of needles resembling iron nitride. This precipitate could be removed by heating for 18 hr. at 500–520° C. Heating at low temperatures (150–180° C.) for periods exceeding 9 days caused reprecipitation.

Metallographic Study of the Formation of Austenite from Aggregates of Ferrite and Cementite in an Iron-Carbon Alloy of 0.5 percent Carbon. T. G. Digges and S. J. Rosenberg. (Journal of Research of the National Bureau of Standards, 1942, vol. 29, Aug., pp. 113–121). A study was made of the nucleation and growth of austenite on heating a high-purity alloy of iron and carbon containing 0.5% of carbon. The changes that occurred in both fine pearlite and an aggregate of spheroidised cementite and ferrite were followed by differentially heating small specimens *in vacuo* at various rates to temperatures within and slightly above the Ac_1 – Ac_3 transformation range and quenching directly in helium. On heating fine pearlite and ferrite, austenite was nucleated at the interfaces of ferrite and carbide, preferentially at the boundaries of pearlite and pro-eutectoid ferrite and at the boundaries of the pearlite colonies. It was also occasionally nucleated within the colonies. Finger-like growths occurred, usually in the direction of the lamellæ, but growths also extended across the lamellæ. During the formation of austenite from fine carbon-poor pearlite, or an aggregate of spheroidised cementite and ferrite, the carbon diffused through ferrite to the austenite grains and also through the austenite during the absorption of the ferrite. Regardless of the rate at which the alloy was heated through the Ac_1 transformation, austenite was nucleated at numerous interfaces of ferrite and carbide, so that, in the initial stages of its formation, the austenite was always fine-grained. However, rapid grain growth may occur in the Ac_1 – Ac_3 transformation range by the absorption or coalescence of the grains initially formed. When the rate of heating through the Ac_1 – Ac_3 range was extremely rapid, this grain growth was largely inhibited, and the resulting austenite was very fine-grained at temperatures considerably above Ac_3 . If heating was less rapid, grain growth was not inhibited and the resulting austenite was very coarse-grained. The dominating factor in establishing the final grain size of the austenite of this alloy was, therefore, the rate of growth, and not the rate of nucleation.

The Solubility of Iron Sulphide in Calcium Sulphide at the Eutectic Temperature. T. Heumann. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 557–558). In an earlier paper by the author and R. Vogel (*see* Journ. I. and S.I., 1942, No. II., p. 36 A) it was stated that iron sulphide and calcium sulphide form a simple system with a eutectic and the possibility of the solid-

solubility of the former in the latter remains open. In the present paper a corrected iron-sulphide/calcium-sulphide constitutional diagram is constructed from data subsequently obtained and the eutectic point is shown to be at 1100°C. , with the composition 12% CaS. The solubility of iron sulphide in calcium sulphide was found by calculation to be 2.1%.

The Iron/Iron-Sulphide/Aluminium-Sulphide/Aluminium Constitutional Diagram. R. Vogel and F. Hillen. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, June, pp. 551-555). The authors established the equilibrium conditions for the iron-sulphur-aluminium system by thermal and microstructural investigations, chemical analyses and the Debye-Scherrer X-ray technique and from these obtained data on the little-known $\text{Al}-\text{Al}_2\text{S}_3$ and $\text{FeS}-\text{Al}_2\text{S}_3$ systems. In the ternary system there is a very large miscibility gap extending from 0.08% Al_2S_3 to 95% Al_2S_3 . The existence of a solid solution on the iron-sulphide side of the $\text{FeS}-\text{Al}_2\text{S}_3$ system was established and the X-ray technique confirmed the hitherto presumed existence of the new double-sulphide phase corresponding to $\text{FeS}.\text{Al}_2\text{S}_3$. Aluminium sulphide solidifies as golden-yellow glass which crystallises on prolonged heating. The ternary system is governed by the liquid miscibility gap which originates in the $\text{Al}-\text{Al}_2\text{S}_3$ system. On the Fe-Al side there is practically no solubility of sulphur from 12% aluminium upwards, and in this it is similar to the iron-manganese system. Thus these equilibria, especially the invariant points, extend into the ternary system at the same temperatures. On the iron/iron-sulphide side the miscibility gap up to 15% sulphur and about 0.5% aluminium approaches the phase boundaries. A small tapering miscibility area is thus formed at the iron corner. Two further miscibility phases were established at the iron-sulphide and aluminium-sulphide corners respectively. Owing to experimental difficulties a closer investigation of the equilibrium conditions of the sulphide side was not made.

ANALYSIS

(Continued from pp. 59 A-61 A)

Fourth Report of the Oxygen Sub-Committee of the Committee on the Heterogeneity of Steel Ingots. (Iron and Steel Institute, 1943, this Journal, Section I). Since the publication of the Third Report of the Oxygen Sub-Committee (see Journ. I. and S.I., 1941, No. I., p. 295 p) the further continuance of the war has interfered with the smooth and regular prosecution of the various researches in hand; several additional problems have, however, been investigated. Considerable attention has been devoted to the determination of gaseous elements other than oxygen, i.e., hydrogen

and nitrogen, as they occur in solid materials. The fundamental aspects of the residue methods and their application to a series of alloy steels have received further examination, and the determination of the gas content of liquid steel, in contradistinction to solid finished products, has been investigated and will continue to be a problem of high priority. The vacuum fusion method continues to be applied to specialised problems such as the surface film on metals. The present Report is in five Sections. The first is introductory.

Section II. is divided into three parts which deal with the determination of oxygen, hydrogen and nitrogen respectively. There are nine papers in Part A of this Section. In the first, H. A. Sloman examines the applicability of the vacuum fusion method to the determination of the oxygen, hydrogen and nitrogen in a series of alloy steels and ferro-alloys used in steelmaking. In the second, T. Swinden, W. W. Stevenson and G. E. Speight report the results of applying the fractional vacuum fusion method to the determination of oxygen in weld metal deposits; from these results it is readily seen that the method furnishes far more information regarding the features of each particular deposit than does the direct total method. In the third, N. Gray and M. C. Sanders describe a modification in the procedure for the aluminium reduction method of determining oxygen in tungsten-bearing steel and in 4% silicon transformer iron. In the fourth, E. W. Colbeck and S. W. Craven describe experiments on the effect of increasing the temperature in the chlorination method on the recovery of oxide inclusions from fully killed steels. In the fifth, T. E. Rooney presents a critical summary of the work carried out on the alcoholic iodine method. The next three papers all relate to the alcoholic iodine method. In the sixth, T. E. Rooney deals with the determination of the water content of methanol and its effect on oxygen determinations by the alcoholic iodine method. In the seventh, G. E. Speight discusses experiments on the composition of extracted non-metallic residues from high-carbon and -phosphorus steels. In the eighth, T. E. Rooney describes the examination and analysis of residues from the alcoholic iodine method. The last contribution to Part A is a note by W. Westwood on oxygen determinations in pig and cast iron by the aqueous iodine method. Part B contains four papers. In the first of these W. C. Newell briefly reviews the development of the present-day methods of determining hydrogen in steel. The other three papers contain detailed descriptions of the apparatus in use at three different laboratories for determining hydrogen by the vacuum-heating method. Thus, W. C. Newell describes that at the Brown-Firth Research Laboratories; W. W. Stevenson and G. E. Speight that at the Central Research Department of The United Steel Companies, Ltd., Stocksbridge; and E. W. Colbeck and S. W. Craven that at I.C.I. (Alkali), Ltd., Northwich. Part C contains three papers all by T. Swinden. In

the first, a general account is given of the principal methods used for the determination of nitrogen in steel. In the second, the general applicability and possible sources of inaccuracy of the vacuum fusion method are discussed. The third contains a brief outline of the development and modifications in procedure recommended for the determination of nitrogen in iron and steel by distillation methods.

Section III. deals with the application of the methods, described in the preceding Section, to several specialised problems. H. A. Sloman and A. J. Cook describe the experimental technique developed at the National Physical Laboratory for the production of low oxygen content iron bar. H. A. Sloman and T. E. Rooney next report on a systematic study of the surface oxygen on different types of specimens of iron and steel by the vacuum fusion and alcoholic iodine methods. T. E. Rooney and F. W. Jones give details of an examination of a number of acid Bessemer, basic Bessemer and basic open-hearth rimming steels by the alcoholic iodine method and of the identification of constituents of the residue by X-ray methods. In an Appendix to the last paper, T. E. Rooney and H. A. Sloman describe the determination of total oxygen by vacuum fusion on a residue prepared by the alcoholic iodine method. W. H. Hatfield and W. C. Newell publish and comment on the results obtained for the gas content of the raw materials used in steelmaking. W. W. Stevenson and G. E. Speight describe experiments with five well-known methods for the determination of oxygen in iron and steel and study their applicability to the determination of oxygen in slag particles in ferrous materials. This is followed by two papers on transformer iron in which N. Gray and M. C. Sanders study the behaviour of 4% silicon transformer iron in the aluminium reduction method in a hydrogen atmosphere, and C. S. Graham and C. W. Short examine the behaviour of this iron in the aluminium reduction method under reduced pressure. Next, J. G. Pearce records the total oxygen contents of twenty-nine pig irons determined by the aluminium reduction method and of seven of the same group by the vacuum fusion method. In the last paper of this Section, T. Swinden presents and comments on the results obtained by the accepted procedures for the oxygen, hydrogen, nitrogen and non-metallic-inclusion contents of a series of alloy steels.

In Section IV. descriptions are given of the methods developed for the sampling of liquid steel and the determination of its gas content, T. Swinden and W. W. Stevenson dealing with the determination of oxygen by a "bomb" method, while W. H. Hatfield and W. C. Newell describe the notched chill-mould method and the balloon-tube method for determining hydrogen.

Section V. consists of a general summary of the Report.

Colorimetric Determination of Boron in Steel Using Quinalizarin Reaction. G. A. Rudolph and L. C. Flickinger. (Steel, 1943. vol,

112, Apr. 5, pp. 114, 131, 149). The addition of very small quantities of boron to steel has led to the need of an accurate method of making boron determinations which would be suitable for the steelworks' laboratory. The authors describe a colorimetric method based on the blue colour formed by boron with quinalizarin in a medium of strong sulphuric acid. No interference in the reaction has been detected when up to 1% of chromium, 1.50% of nickel and 0.50% of molybdenum were present. An experienced chemist can make 15 to 20 determinations in 8 hr. by this method, full details of which are given.

The Determination of Aluminium in 25% Ni-10% Cr-1% Al Steel. E. C. Pigott. (Iron and Steel, 1943, vol. 16, May, pp. 325-327). In a recent paper S. D. Steele and L. Russell (*see* Journ. I. and S.I., 1943, No. I., p. 228 A) described some modifications of the present author's method of determining aluminium in nickel-chromium steels and advocated the preliminary removal of the interfering elements chromium and nickel. In this paper the author describes his procedure for determining aluminium in 25/10 nickel-chromium steels by the original method of converting the iron and alloying elements to non-interfering ferrocyanides in ammoniacal tartrate solution from which the aluminium is directly precipitated as an oxine complex.

Determining Open Hearth Residuals by Routine Spectrographic Analysis. J. T. Rozsa. (Iron Age, 1943, vol. 151, Mar. 11, pp. 58-62). The author discusses the advantages of the spectrographic method for the detection and determination of residual elements in samples of open-hearth steel; these elements occur more frequently in war-time owing to the wide variety of scrap metal which is now melted down. The layout of a modern laboratory with dark room for spectrographic work is described in detail.

ORES—MINING AND TREATMENT

(Continued from pp. 65 A–66 A)

The Italian Iron-Bearing Sea Sand, Its Preparation and Use. (Stahl und Eisen, 1942, vol. 62, Dec. 3, pp. 1034–1035). Brief details are given of the progress made in the beneficiation and smelting of ferruginous sands on the coasts of Italy. At Ladispoli, near Ostia, where the deposits stretch 50 m. inland and are 2 m. deep, one mobile and two stationary magnetic separators are already in operation. About 200 tons of concentrates containing 95% of magnetite are produced daily. When the necessary plant is completed the sandy concentrates are to be sintered in a continuous unit rated for an output of 550 tons of sinter per day, lignite coke being used for both sintering and smelting in the electric furnace. It is proposed to transfer the liquid iron from the electric smelting furnaces *via* a mixer to open-hearth furnaces, which are to be heated with the gas obtained from the electric furnaces. Two acid converters are to be erected to produce Bessemer steel. (An abridged English translation of this article appeared in Iron and Coal Trades Review, 1943, vol. 146, Apr. 30, p. 650).

New Process for Treatment of Low-Grade Chromite Ores. (Mines Magazine, 1942, vol. 32, Aug., pp. 385–386). Brief particulars are given of a process of concentrating low-grade chromite ore from vast deposits which have been discovered in Montana. The process has been developed by the Bureau of Mines. The ore is mixed with coke and treated in a rotary kiln; most of the iron-bearing portion is then removed by either gravity concentration or magnetic separation with subsequent leaching with sulphuric acid.

Sintering Plant for Fine Ores. (Engineering, 1943, vol. 155, June 18, pp. 486–487). A brief illustrated description is given of the new sintering plant at the works of the Youngstown Sheet and Tube Co., Ohio, which has a daily rated output of 2400 short tons of sinter (*see* Journ. I. and S.I., 1943, No. I., p. 189 A).

REFRACTORY MATERIALS

(Continued from pp. 66 A–68 A)

Furnace Gas Pressure as Affecting the Life of Refractories. S. M. Phelps. (American Refractories Institute: Heat Treating and Forging, 1943, vol. 29, Apr., pp. 193–196). The author describes an investigation of the effects of changes in furnace gas pressure on two brands of high-duty firebricks. The test panels consisted of fourteen 9-in. bricks set with kaolin mortar and backed with insulat-

ing bricks. The test temperature of 2910° F. on the hot face was reached in 6 hr. and then maintained for 24 hr. Changes in pressure were obtained by sealing a sheet-metal hood over the outside surface of the insulating bricks. This hood could be connected to either the suction or delivery side of a blower, so that the pressure or suction could be applied to the outside of the panel. At a pressure of $+\frac{1}{2}$ in. of water on the hot face of the bricks the temperature at the junction of the firebrick and insulating brick was 2265° F., at the outside of the insulating bricks 400° F., and the spalling loss was 12.9%; the corresponding values at $+1\frac{3}{4}$ in. of water were 2365° F., 620° F. and 20.2%; at $-1\frac{7}{8}$ in. of water they were 1060° F., 195° F. and 2.9%.

The Maintenance of the Furnace Linings in Large Basic Open-Hearth Tilting Furnaces by the Use of Chrome Ore, Magnesite and Serpentine. A. Jackson. (Iron and Steel Institute, 1943, this Journal, Section I). In a recent paper, "The Linings of Large Basic Open-Hearth Tilting Furnaces" (see Journ. I. and S.I., 1942, No. II., pp. 9 F-16 F) developments in economising in the use of magnesite bricks for large open-hearth tilting furnaces were described. This included discussion of the usefulness of stabilised dolomite bricks, the importance of the quality of "Basic" and reduction in the number of chrome-magnesite bricks used in front walls. The information then given is now supplemented by a discussion of the use of parging pastes containing chrome ore and serpentine, with the object of reducing still further the consumption of magnesite. The possibility of reducing the consumption of chrome ore is also considered. Results obtained with various mixtures of magnesite, chrome ore and serpentine are described.

Electric Steel Plant Refractories. J. H. Chesters. (Iron Age, 1942, vol. 149, Mar. 4, pp. 37-43, 104, 105). The author describes four methods of lining electric furnaces using: (1) Pre-formed crucibles; (2) the steel-liner method for monolithic linings; (3) the asbestos-liner method for monolithic linings; and (4) acid or basic bricks. In a monolithic lining the grading of the material is by far the most important factor. The following grading is a safe, but not necessarily ideal, mixture for all induction furnace linings: 45% in the range of British Standard sieves 7-25, 10% B.S. sieves 25-72, 20% B.S. sieves 72-150 and 25% through B.S. sieve 150. Quite satisfactory basic linings for small furnaces can be made with either straight magnesite or magnesite bonded with 1% of boric acid. For a 2-ton furnace the following composition has been found to give excellent service: MgO 73.5%, CaO 5.4%, Al_2O_3 2.4%, Fe_2O_3 7.1% and SiO_2 8.2%; the remaining 3% consists of impurities and bonding materials. "Electrically fused magnesia which is very pure (MgO over 92%) gives no better life than ordinary dead-burned magnesite and, in tests, the shrinkage cracking was worse than usual. The fine fraction in the grading is very important, as it promotes good sintering; linings with only 5% "through 120 mesh" failed

in the first melt due to lack of sintering in the top section. The resistance of 70-30 magnesia-zircon linings to slag is much less than that of straight magnesite, but the former has a positive expansion on firing and shows no shrinkage cracking. Trials have been made with unfired curved tiles pressed mechanically, and a life about twice that of monolithic linings is claimed for them.

FUEL

(Continued from pp. 68 A-70 A)

Automatic Combustion Control for Steel Plant Boilers. M. J. Boho. (Blast Furnace and Steel Plant, 1943, vol. 31, Apr., pp. 430-434, 447, 448). The author describes a typical automatic combustion control layout at a steelworks' boiler plant fired with blast-furnace gas with auxiliary coal fuel when necessary.

Waste-Heat Recovery in Steelworks. L. R. Broome. (Iron and Steel, 1943, vol. 10, May 20, pp. 352-356). The author presents calculations relating to the economy of waste-heat recovery in steelworks. In an example of a producer-gas-fired open-hearth furnace making 1400 tons of steel per week, the steam produced was 1,965,000 lb. at 212° F. and higher, and, on the basis of 9 lb. of steam per lb. of coal, the coal saving was about 100 tons per week. For soaking-pits and reheating furnaces the recovery should be about 2 lb. of steam from and at 212° F. per lb. of coal feeding the gas producers. A suitable boiler should comply with the following conditions: (1) Good heat transfer by convection; (2) be easy to clean on the fire side and the water side; (3) have a good water content; (4) have a low resistance; (5) have an ample reserve of fan power; and (6) be compact and self-contained with no brick setting. The boiler which best satisfies these conditions is the fire-tube boiler in which the gases are drawn through the tubes by an induced draft which may be either electrically or steam driven. Data are presented on the results of trials on two waste-heat boilers working in conjunction with two 90-ton open-hearth furnaces.

New Developments in the Field of Coal Preparation. H. P. Nicholson. (Illinois University, Engineering Experiment Station, 1942, Circular Series No. 43, pp. 19-24). The author discusses some aspects of cleaning Illinois coals for local markets. The present trend is towards the heat drying of an increased amount of washed coal to overcome the problem of freezing in transit and to avoid paying freight on the moisture in coal.

New Developments in Air Cleaning of Coal. W. C. McCulloch. (Illinois University, Engineering Experiment Station, 1942, Circular Series No. 43, pp. 25-28). Some pneumatic machines for cleaning coal are briefly described. These may be classified in three

groups: the air-flow or launder type; the air-sand type and the reciprocating table type. In the first, the only motion necessary for the cleaning is provided by the pulsating air current, the moving distributing plate and the air valve levers. The surface of the perforated metal is smooth and does not impede the forward movement of the stratified material. In the air-sand type, the fine sand is made fluid by air bubbled through the sand; the fluidity of the resulting medium spreads the coal in a thin layer, so that rapid separation of coal and impurities takes place. Air distribution is controlled over the separating area by porous filtering blocks which are moulded to form the bed of the separator box. In the reciprocating-table type the perforated screen is corrugated; the refuse is retained between the corrugations, and is propelled towards the end of the machine. The clean coal flows transversely over the top of the corrugations aided by adjusting the tilting deck; middlings can be diverted and recirculated if desired.

Ash Control in Coal Washing Plants. W. J. F. Moran. (Illinois University, Engineering Experiment Station, 1942, Circular Series No. 43, pp. 29-34). The author describes a procedure for making rapid determinations of the percentage of ash in coal. The sample is ground to about 10 mesh, dried for about 4 min. at 400° F. and reduced to 60-mesh size through a rotary disc pulveriser. A 1-g. sample is placed in a combustion boat in a small electric combustion-tube furnace, in which it is completely oxidised in 5 min. with the aid of a stream of oxygen; the boat is withdrawn from the furnace, cooled and weighed. By using a tared weighing pan to weigh both the sample and the ash, and having rapid communication between the coal-cleaning plant and the laboratory, the ash determinations can be given to the plant operators 20 min. after collecting the samples.

The Curran-Knowles Coke Oven. M. D. Curran. (Iron and Steel Engineer, 1943, vol. 20, Apr., pp. 45-47). The Curran-Knowles oven was originally designed for making a smokeless fuel from Illinois coal of low coking capacity. The oven is horizontal with sole flues. It is made of fireclay brick, except for the flues, which are of silica brick. The gases leave the oven at about 700° F., and this permits small unlined stand-pipes to be used. Regenerators are incorporated beneath the flues, and they lower the temperature of the products of combustion from 2500° F. to 500° F. Heat recovery is also applied to the coke-oven gas. The power required to push the oven is only about a quarter of that necessary for vertical ovens. The coke is discharged on to a metal plate conveyor, which carries it to the quenching station. Heating the coal from the underside causes the fusion zone to travel upwards, driving the volatile constituents before it; these are condensed in the cooler coal above and are redistilled several times during the carbonising process. Since the gases escape without being subjected to cracking, there is a high yield of tar per ton of coal.

Carbonization of Coal by the Disco Process. C. E. Leshner. (Illinois University, Engineering Experiment Station, 1942, Circular Series No. 43, pp. 35-40). The author describes the Disco low-temperature carbonisation plant of the Pittsburgh Coal Carbonisation Co. In this process, preheated finely divided coal mixed with coke breeze pass down an inclined revolving retort which is surrounded by a stationary shell insulated on the outside. By-product gas in controlled amounts is burned and mixed with recirculated gas so that the mixture is at about 1020° F.; this gas is forced through the annular space surrounding the retort at about 3500 cu. ft. per min. The coke yield ranges from 63% to 75% on a dry-weight basis. The tar yield is from 15 to 30 gallons. Disco coke has a true specific gravity of 1.456 and a porosity of 41.2%.

PRODUCTION OF IRON

(Continued from pp. 71 A-72 A)

Principal Factors Affecting the Life of a Blast Furnace. W. A. Haven. (American Iron and Steel Institute: Industrial Heating, 1943, vol. 10, Apr., pp. 570-574). The author discusses briefly the improved life of blast-furnace linings which has been obtained from the combined effects of using sinter, better distribution of the charge since the introduction of the revolving top and improvement in the quality of the refractory bricks.

Increasing Blast-Furnace Efficiency with a Simultaneous Saving in Coke. E. Senfter. (Iron and Steel Institute, 1943, Translation Series, No. 139). This is an English translation of a paper which appeared in *Stahl und Eisen*, 1942, vol. 62, Dec. 10, pp. 1041-1052. (See Journ. I. and S.I., 1943, No. I., p. 120 A).

The Combustion of Coke with Oxygen-Enriched Blast and Its Effect on Smelting. R. Durrer, P. Lwowyecz and B. Marínček. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 329-332). In previous experiments (see Journ. I. and S.I., 1941, No. II., p. 38 A) R. Durrer had observed that when coke was burned with pure oxygen there was a considerable amount of carbon dioxide in the products of combustion. The explanation offered was that the quantity of gas formed was too small to raise the temperature of the surrounding zone to a point sufficiently high for reduction of the primary carbon dioxide to carbon monoxide to take place. The present authors describe a further investigation of this subject using a small shaft furnace 20 cm. in dia. with two tuyeres, a coke with 1.1% of ash, and blast in which the proportion of oxygen was 21%, 42%, 66% and 100% in different tests. Contrary to the previous observations, it was noted that increasing the proportion of oxygen in the blast promoted the reduction of carbon dioxide to

carbon monoxide. The rate of this reaction depends greatly on the temperature, other conditions being equal. The reaction rate in the first stage (that of carbon dioxide formation) is slower with air only than with oxygen-enriched blast. A high initial temperature has a greater effect on the reduction of the carbon dioxide than a steep temperature drop. The experiments indicate that it would be possible to operate a low-shaft furnace with an air blast the gases from which would consist of nitrogen and carbon dioxide only. Full-scale tests would be necessary to test the smelting efficiency of such a furnace; an advantage would be that a cheap fuel of low physical strength would be able to support the reduced weight of the burden. There seems to be no practical way of obtaining complete combustion of all the carbon, so that a mixture of carbon monoxide and carbon dioxide must be counted on. An increased proportion of the former means a higher fuel consumption in the furnace, but the flue gas would have a higher calorific value. If a burden requiring 750 kg. of coke to produce 1000 kg. of iron in an ordinary blast-furnace were used in a low-shaft furnace, the carbon required to produce 100% of carbon monoxide in the flue gas would be about 1500 kg. per ton of iron, and this would need 1200 cu. m. of oxygen, to which the ore would contribute about 300 cu. m. The blast would therefore have to supply about 900 cu. m. of oxygen per 1000 kg. of iron, and this would increase the cost of the iron by about 10 R.M. per 1000 kg.

Sintering Plant Practice and the Use of Sinter in the Blast Furnace.

M. E. Nickel. (Eastern States Blast Furnace and Coke Association: Blast Furnace and Steel Plant, 1943, vol. 31, Apr., pp. 65-S-71-S). The author presents and discusses data relating to the production and use of sinter at the Wisconsin Steel Works, South Chicago. During 1942 the sintering mixture was gradually changed from 81% of flue dust with 18% of fine ore to 32% and 58% respectively, and this caused the production per day to increase from 729 tons to 1051 tons. An addition of about 3% of open-hearth slag screenings gave the charge more porosity and raised its manganese content. The sinter contained about 58% of iron, 0.73% of manganese and 12.67% of silica. Increasing the proportion of sinter in the total burden beyond 20% did not increase the production of iron and caused irregular furnace operation. The maximum iron production was obtained with about 20% of sinter. One furnace was run with 45% of beneficiated ore in the burden and no sinter, and a similar furnace was run with no beneficiated ore and 44.7% of sinter; the average daily production was 784 tons for the first and 727 tons for the second furnace.

FOUNDRIY PRACTICE

(Continued from pp. 72 A-76 A)

Effect of Moisture in Blast Air. R. J. Cowan. (Iron Age, 1942, vol. 150, Nov. 12, pp. 43-50; Nov. 19, pp. 46-50). The author discusses the use of blast with a controlled moisture content for cupolas, blast-furnaces and converters. A chart is presented showing the additional amount of coke required in a cupola charge to compensate for increases of from 1 to 20 grains of moisture per cubic foot of blast. As the moisture content increases, the total carbon content of the metal decreases, the silicon content decreases and the combined carbon increases considerably. In the case of chill-cast iron, the chill depth is greater with increasing moisture in the blast. A brief description of the Kathabar dehydration unit is given; this employs lithium chloride for absorbing the moisture.

Cupola Melting of Loose Cast-Iron Borings. S. L. Feduska. (Metals and Alloys, 1943, vol. 17, Feb., pp. 316-319). The author describes a method developed at an American foundry for melting cast-iron borings in a 45-in. cupola. An acute shortage of chromium-molybdenum iron scrap, low in phosphorus, arose, and the only solution was to make use of the borings from the foundry machine shop. The quantity did not justify the installation of a briquetting plant. It was found best to melt with a blast pressure of 6-10 oz., maintaining a stock height of $4\frac{1}{2}$ - $5\frac{1}{2}$ ft., with charges consisting of 1500-2000 lb. of turnings, 150-200 lb. of coke, and 35 lb. of limestone. The amount of metal lost was less than 5%. Using turnings containing total carbon 3.14%, silicon 1.09%, manganese 0.44%, chromium 0.82% and molybdenum 0.35%, the proportion of the elements lost in the iron produced was silicon 25%, manganese 50%, chromium 25% and molybdenum 25%. In one case only the carbon content dropped to 2.56%. The volume of slag was greater than with normal charges, but it had a much lower density. The erosion of the lining was slightly more than normal. It is expected that a melting rate of 8 tons of boring per hr. will be obtained in this cupola.

An example of English practice with a 33-in. dia. balanced blast cupola is quoted in which 6-7 tons of loose iron borings are melted per day. Two charges of 500 lb. each of heavy scrap are put on the coke; the level of the stock is then maintained with charges of 400 lb. of loose borings, 200 lb. of pig or scrap, 100 lb. of coke, 75 lb. of limestone and 50 lb. of silica sand.

Basic Cupola Process for Desulphurisation. E. S. Renshaw. (Foundry Trade Journal, 1943, vol. 70, June 24, pp. 149-153). The author reports on trials with a 27-in. cupola in which a basic lining was substituted for the usual acid refractory in order to increase the

basicity of the slag and use it for desulphurising instead of resorting to the soda-ash process. Dolomite bricks 1 in. thick were placed against the shell, followed by $3\frac{1}{2}$ in. of rammed stabilised dolomite cement mixed with 6% of water and 1% of sodium silicate. The lining was first air-dried and then heated with a gas flame, the temperature being increased to 400° C. in 10 hr. For repairs to the melting zone, a patching cement was prepared by grinding stabilised dolomite clinker to a finer grading than the ramming material. The patching cement was milled with about 12% of water; this must be applied immediately after mixing, as it possesses air-setting properties. A continuous tapping box through which both slag and metal passed was rammed with the same material. The box had a teapot spout for the metal and a slag notch at the side. In operation, the cupola well carried a relatively large volume of slag with a minimum quantity of metal. The coke-bed was 42 in. above the top tuyeres. The coke analysis was: fixed carbon 90%, sulphur 0.90%, ash 9.5% and volatile matter 0.50%. The flux consisted of limestone and fluorspar, the latter to make the slag fluid enough to flow over the slag notch. In the experimental melts the proportion of steel charged was progressively increased to 100%. With a charge of 100% grey iron scrap the sulphur in the charge was 0.12%, and in the metal tapped this was reduced to 0.056%. In the remaining melts with increasing steel and representative of mixtures suitable for making low carbon irons, malleable iron and Tropenas converter steel, the desulphurisation was sufficient to obviate any after-treatment with soda ash. The trials having been successful, a 36-in. cupola was lined with the same material. The continuous tapping system was employed, the metal flowing into an electric furnace the inlet of which was only 4 ft. from the cupola tapping hole. Over 3000 tons of metal have been melted in this cupola, but figures on the consumption of refractory material are not yet available.

Meeting the Raw Materials Supply Position in Grey Iron Foundries. (Institute of British Foundrymen, Fortieth Annual Conference, June, 1943, Paper No. 772). This paper is a report by the Cast Iron Sub-Committee of the Technical Committee of the Institute of British Foundrymen, issued with the object of assisting foundrymen in maintaining quality of output while using raw materials of lower grade. The scarcity of low-phosphorus iron has been met by: (a) Using pig-iron with about 0.4% of phosphorus instead of hematite-iron in cupola charges; (b) replacing hematite with refined pig-iron; (c) careful control over the metal mixture, in particular over the carbon and silicon, whereby the deleterious effects of phosphorus on the mechanical properties can be counterbalanced; (d) careful attention to improved methods of gating and risering; (e) adopting centrifugal casting methods whenever possible; (f) careful attention to the pouring temperature; and (g) the correct use of denseners. Several examples of the methods advocated are described and illustrated.

Some Aspects of the Production of Malleable Iron Castings.

J. Roxburgh. (Institute of British Foundrymen, Fortieth Annual Conference, June, 1943, Paper No. 770). The author describes the moulding; gating and feeding practice at Ley's Malleable Castings Co., Ltd. Bentonite was formerly used as a bond, but when this became unobtainable, Fulbond No. 1 was substituted. The synthetic sand, after milling, is put through a disintegrator; this helps to spread the bond over the grains of silica sand, and has resulted in less frequent "pulls" or "hot tears" on the castings. Spherical-shaped feeders are used with success; these have the least surface area to dissipate heat from a given volume, and good castings were produced with a minimum amount of metal for feeding. With some feeders the bottom half of the feeder is dispensed with and a feeder shaped as a cylinder with a hemisphere on top is used; this type is useful when joined to a vertical wall of metal. To prevent the loss of heat from the surface of feeders on top of a casting, the feeder is also made spherical in shape; the bottom hemisphere is moulded, and the top hemisphere formed in a core with a hole in the top through which metal can be added.

Pearlitic Malleable Cast Irons. A. E. Peace. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, June 10, pp. 109-114; June 17, pp. 129-134). The author explains the mechanism of graphitisation in the making of malleable iron. The graphitisation taking place while obtaining equilibrium at the maximum temperature is known as first-stage graphitisation, and that occurring on cooling to below the critical point as second-stage graphitisation. If blackheart malleable iron is reheated above the critical temperature, temper carbon will go back into solution, the amount redissolved depending on the temperature and time. The iron thus produced is known as pearlitic malleable; in this case the redissolved carbon diffuses first of all along the grain boundaries, so that after a short period at above the critical point a network structure is obtained in a ferrite matrix. The re-solution of some of the free carbon by reheating above the critical point is also used to produce surface hardening by means of flame and induction heating; by such a process a martensitic structure is obtained in the surface with a hardness equivalent to that of case-hardened steel. There is some evidence that oxygen may accelerate graphitisation by nucleation. It is also possible that oxide films may retard graphitisation. It is established that oxygen-contaminated cementite is stable under annealing conditions and will not dissociate into iron and carbon. The arresting of second-stage graphitisation can be effected by alloying elements. About 0.1% of vanadium effectively prevents decomposition of the carbide, but the cementite structure is so massive that shock resistance is poor. Manganese has been utilised in quantities of 0.5-1% above the amount normally present. To obtain a completely spheroidised structure with manganese it is necessary to cool rapidly through the critical temperature and then

hold at just below it for some hours. The effect of molybdenum is more drastic than that of manganese, but less than that of chromium. Copper and nickel have been used for their effect upon the matrix structure as distinct from the effect on graphitisation. Second stage graphitisation proceeds further with increasing quantities of nickel, so that structures which would normally be all pearlitic contain appreciable quantities of ferrite. Data on the physical properties of pearlitic malleable iron are presented.

Converting to Steel Castings. J. H. Smith. (Iron Age, 1943, vol. 151, Apr. 22, pp. 45-50). The author describes the conversion from the production of malleable iron castings to that of 2500 tons of steel castings per month at the Saginaw Malleable Iron Division of the General Motors Corporation. The methods used successfully in making malleable iron were adapted to steel casting production instead of changing over to conventional steel-foundry procedure. In a normal 24-hr. day, twenty 8-ton heats and ten $3\frac{1}{2}$ -ton heats are tapped from acid electric furnaces. Steel is poured into the moulds from 5-cwt. teapot ladles carried by electric hoists on an overhead monorail. For some castings produced in large quantities an automatic burner has been devised for the rapid removal of the sprues and risers. The high rate of production is largely due to the extensive use for well-designed conveying equipment.

Cast Steel Chain. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, Apr., pp. 18-19). A description is given of the method employed by Sorel Steel Foundries Ltd. to make $1\frac{1}{4}$ miles of cast steel chain with links of bar $2\frac{1}{4}$ in. in dia. An electric furnace steel with carbon 0.45-0.50% and manganese 1.50-1.75% was used. Single links were cast first and these were prepared in sets of eight for pouring the connecting links; these were poured through a single pouring gate, but each link had its own riser. The heat treatment consisted of cooling in the furnace from 1650° F., reheating to 1560° F., quenching in oil and then tempering at 1150° F.

Hot Tear Formation in Steel Castings. C. W. Briggs. (Institute of British Foundrymen, Fortieth Annual Conference, June, 1943, Paper No. 774). The author considers the causes of hot tears in steel castings. The strength of the sand and cores can be sufficient to hinder the contraction of the casting in the mould and set up high stresses causing hot tears. While the sand at the mould face is at about 2500° F. and has a strength of perhaps 20 lb. per sq. in., that at a depth of only $\frac{1}{8}$ in. from the casting is at 2000-2200° F. and has a strength of perhaps 1000 lb. per sq. in. For steel castings the maximum hot strength of the sand at 2500° F. ought not to exceed 25 lb. per sq. in. With two similar castings produced under similar conditions in 0.15% carbon steel and 0.45% carbon steel, at 2300° F. with hindered contraction, a stress of 750 lb. per sq. in. can be expected in the former and one of 500 lb. per sq. in. in the latter. It might be considered, therefore, that low-carbon steel is more liable

to develop hot tears, but this steel has 1.4 times the tensile strength and 8 times the ductility of the high carbon steel at 2300° F. Also, the temperature range for hot tear formation is much smaller in low carbon than in high carbon steel. The two types cannot, therefore, be compared directly with regard to susceptibility to hot tears.

A Wartime Steel Foundry—Some Problems and Developments. E. D. Wells and A. Johnson. (Institute of British Foundrymen, Fortieth Annual Conference, June, 1943, Paper No. 776; Foundry Trade Journal, 1943, vol. 70, July 8, pp. 199-202, 204; July 15, pp. 221-224). The authors discuss experiences in steel foundry practice under war-time conditions. Using Poumay cupolas which have small main tuyeres and subsidiary preheating tuyeres, the maximum proportion of steel scrap in the charge was 90%, the other 10% consisting of 4-5%-silicon iron; such a high percentage is only possible with scrap of the best quality. The Perrin process of dephosphorisation was tried on metal containing 3.5% of carbon; slag was melted in an electric furnace and the cupola metal tapped on to it from a considerable height; a violent reaction started immediately and both slag and metal boiled out of the ladle. The dephosphorisation achieved was negligible and the experiments were discontinued. A lining of ground stabilised dolomite made up with 6% of water and rammed round a former was tried for the desulphurising ladle in the soda-ash process; the results showed better average desulphurisation, greater regularity, but a poor lining life, rendering this material uneconomical. Experiments are in hand using unstabilised dolomite bonded with tar and it is believed that a very satisfactory basic lining for desulphurising ladles will be developed. The advantages of using the whirlgate head are: (1) The better positioning of the heads and the small ingates means less oxy-acetylene cutting and grinding on the castings; (2) an increased yield of castings from a given amount of liquid steel can often be obtained by feeding up to four small castings from one centrally placed whirlgate head; (3) by taking advantage of the temperature gradients of the steel, smaller heads can be used; and (4) cleaner castings can be produced.

The Continuous Production of Manganese Steel Castings from the Tropenas Converter. L. W. Bolton and J. Hill. (Institute of British Foundrymen, Fortieth Annual Conference, June, 1943, Paper No. 775). Austenitic manganese steel with 11-14% of manganese can be made from a dead mild steel, produced by means of the cupola and Tropenas side-blown converter, and adding to it the requisite amount of molten ferro-manganese. The problem of having manganese steel available for small castings at a continuous casting plant without using a holding furnace is solved by taking a weighed quantity of molten metal, sufficient for a heat, from a cupola and transferring it to a Tropenas converter; while this is being converted, a weighed quantity of ferro-manganese is taken from a cupolette and transferred to the pouring ladle; the steel from the

converter is teemed on to the ferro-manganese and the ladle is then taken to the pouring station in the foundry. A detailed description of the practice at a plant with two converters, of 25-cwt. and 24-cwt. capacity respectively, is given. The blowing time increased with increasing silicon content, the time tending to increase more rapidly after the silicon content reached 1.5%. The time elapsing before the appearance of the flame increased with the silicon content, and, after the appearance of the flame, the blowing time varied very little and was generally 8 to 10 min.

Permeability Testing. R. C. Tucker. (Foundry Trade Journal, 1943, vol. 70, June 10, p. 115). The author describes a modification of the British Cast Iron Research Association apparatus of testing the permeability of sands. The B.C.I.R.A. tester will not allow the measurement of the permeability of a dried or baked core with a mercury seal, as the core holder would be upside down. Baked cores can be tested in the modified apparatus.

Centrifugal Casting. N. Janco. (American Foundrymen's Association: Iron Age, 1943, vol. 151, Apr. 22, pp. 51-54). In the centrifugal casting of steel the mould should spin on a horizontal axis for cylindrical castings when the length greatly exceeds the diameter. When the length is equal to or less than the diameter a vertical axis can be used, but the inside diameter of the casting will be less at the bottom than at the top; in practice the amount of taper cannot be materially reduced by rotating at speeds exceeding 1500 ft. per min. at the periphery.

The Development of Centrifugal Casting. C. W. Briggs. (Steel Founders' Society of America: Iron Age, 1943, vol. 151, May 13, pp. 53-55). The author explains the principles of centrifugal casting and discusses some examples indicating the applications of moulds spinning on a horizontal and on a vertical axis.

Centrifugal Casting with Vertical Spindle Machines. P. C. Power. (Steel Founders' Society of America: Iron Age 1943, vol. 151, May 13, pp. 55-57). The author describes some of the vertical spindle centrifugal casting machines of the Maynard Electric Steel Casting Co., Milwaukee. Two sizes of spinner tables (36 in. and 46 in. in dia.) driven by 3-h.p. motors are used. By using pulleys of different sizes the spindle speed can be adjusted between 50 and 450 r.p.m. The castings produced vary between 30 and 500 lb. in weight and the flask sizes range from 20 × 20 in. to 38 in. in dia. The average yield of castings is about 80% of the steel in the electric furnace heat.

Centrifugal Casting in Vertical Machines. A. T. Baumer. (Steel Founders' Society of America: Iron Age, 1943, vol. 151, May 13, pp. 57-58). The author gives some particulars of the vertical spindle centrifugal casting machines at the works of the Wehr Steel Co. Clusters of five cast bushes are made at a time, the cores being evenly distributed round a central sprue. The top section of the casting is cast in a permanent mould die which serves as a permanent core.

The Hows and Whys of Centrifugal Casting. H. B. Zuehlke. (American Foundrymen's Association, Forty-seventh Annual Meeting, Apr., 1943, Preprint No. 43-2). The author discusses the advantages of centrifugal casting and presents formulæ with which the degree of taper in the bore of cylindrical castings can be calculated for any desired position of the axis of the spinning mould.

PRODUCTION OF STEEL

(Continued from pp. 77 A-78 A)

Sanderson Brothers & Newbould Ltd.; Steelmakers for 167 Years. (British Steelmaker, 1943, vol. 9, July, pp. 280-290). A historical account is given of the development of the Sheffield firm which has been known since 1901 as Sanderson Brothers and Newbould Ltd., makers of crucible cast steel tools and rolled bars. The firm was founded in 1776 by Thomas Sanderson in partnership with George Naylor.

The Development of Personnel in the Steel Industry. R. J. Greenly. (Iron and Steel Engineer, 1943, vol. 20, Apr., pp. 19-24). The author considers the problem of recruiting and training labour for the steel industry in the United States. Instead of attempting to estimate the number of workers that will become available when the production of non-essential materials is still further reduced, steelmakers should collaborate with the management of such industries in their own district. A survey of the existing labour should be made to discover men whose skill is not being exploited with a view to promoting them and replacing them with unskilled men or women. Apprenticeship training does not lend itself to the present urgent need for labour in steelworks, whereas job training, supervisory training and trade extension training produce much more rapid results. In the conference method of training supervisors an educational committee, or training advisory council, should be established which would consist of the leading operating superintendents. The director of training should meet this group and help to develop and coordinate the program.

Controlling the Heating-Up of Open-Hearth Furnace Arches. F. Strähuber and R. Klesper. (Stahl und Eisen, 1943, vol. 63, Mar. 25, pp. 236-239). The authors describe methods of heating-up open-hearth furnaces, giving examples of the arrangement of gas burners and thermocouples for the supply of heat and temperature measurement and reproducing suitable temperature schedules. They recommend heating to 400° C. at a steady rate of 10° C. per hr. and from 400° to 1600° C. at not more than 25° C. per hr. Data on the expansion of silica brick at different temperatures are presented.

The Optimum Position for the Zero Pressure Line in Open-Hearth Type Furnaces. A. H. Leekie. (Journal of the Institute of Fuel, 1943, vol. 16, Apr., pp. 127-129). In the operation of open-hearth furnaces opinions differ on the extent to which flame should escape from the upper part of an open furnace door and cold air be drawn in through the lower part, in other words, at what position of the zero furnace pressure level is there the least loss of heat. The author develops formulæ for calculating the heat losses through the escape of flame and the infiltration of air and explains how the optimum position of the zero pressure line can be determined.

The Development of Research and Quality Control in the Modern Steel Plant. L. F. Reinartz. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1593: Metals Technology, 1943, vol. 10, Apr.). The author discusses the growth of research work and of methods of control applied to steelmaking in the United States. The extensive research facilities at the works of the American Rolling Mill Co., and the methods this company has adopted to control output and secure uniform quality are briefly described. A specimen of an open-hearth furnace log is reproduced. The blast-furnace department is asked to supply hot metal containing 0.70-1.00% of silicon, sulphur 0.030% max., and phosphorus 0.300% max. The metal is tapped at 2650-2750° F. at the Hamilton plant of the above company and is transferred in special 175-ton bogie trucks 12 miles to the Middletown plant, during which time the temperature falls about 50° F. The hot metal makes up 50% to 75% of the open-hearth furnace charge; it is treated in the transfer trucks with a predetermined amount of mill-scale which brings the silicon and manganese contents down to the desired level. Close control is exercised over the casting-pit practice, soaking pits, rolling and all subsequent stages right up to the despatch department.

The Basic Open Hearth, Modern Plant and Practice. J. A. Davies. (Journal of the West of Scotland Iron and Steel Institute, 1942-43, vol. 50, Part IV., pp. 39-43). The author describes modern basic open-hearth plant and practice. In straight coke-oven gas furnaces working the Hoesch system, the gas is usually fed to the furnace ends by water-cooled burners 3½ in. in dia. The gas being projected at a velocity of approximately 250 ft. per sec. into a relatively slow-moving air stream gives great turbulence and a high temperature. If the regenerated air is at 1200° C., a flame temperature approaching about 2800° C. is attained. The complicated mechanism of straight through reversing valves is not very good on hot dirty gas; a Drum or Forter valve is quite satisfactory provided that the areas are adequate for the size of the furnace and that the furnace is coupled to a boiler with an adequate fan. Instruments should be provided for: (a) Recording the flow of the fuel gas; (b) recording the temperature at the top of the chequers; (c) recording the gas temperatures before and after the waste-heat boilers; (d) recording the draft in between the furnace and boiler; and (e)

indicating the difference in draft between positions before and after the boiler. At one of the furnaces described the checkers were made up of common firebrick for the bottom third, 40% alumina brick for the middle third and first-grade silica brick for the top; later the silica bricks were eliminated and the alumina bricks carried right to the top; the high-alumina bricks were found to be more resistant to slagging from basic furnace dusts.

Turnings Charged with Pusher Boxes. (Iron Age, 1943, vol. 151, Apr. 29, pp. 44-45, 117). Particulars are given of the method adopted by the Republic Steel Corporation to charge turnings into open-hearth furnaces. Large welded charging boxes with a capacity of 106 cu. ft. were made, and the furnace doors had to be enlarged. These boxes had the disadvantage that they could only be used in the early stages of charging owing to lack of roof clearance. Another method was to construct one charging box of 224 cu. ft. capacity across the charging car; one end of this formed a gate which could be lowered into the furnace door, and the other end could be pushed forward by the ram of the charging machine, thus discharging the turnings into the furnace.

Open-Hearth Slag Control for Manganese. C. F. Quest, A. E. Martin and T. L. Joseph. (Metals and Alloys, 1943, vol. 17, Apr., pp. 767-769). The authors report on laboratory experiments to determine the distribution of manganese between slag and metal using 500-g. melts of open-hearth ingot iron in a rotating induction furnace. Three series of slags with lime/silica ratios of 0.92, 1.29 and 1.64 were investigated at temperatures in the 1565-1675° C. range. A 15-g. briquette of slag was added immediately after melting down and putting in the electrolytic manganese. After 1 hr. at the temperature selected the slag was removed, the metal bath was killed with aluminium, cooled, sampled and analysed. The manganese equilibrium constant fell steeply at lime/silica ratios between 1.29 and 1.64. The conclusions of L. S. Darken and B. M. Larsen were confirmed (see Journ. I. and S.I., 1943, No. I., p. 49 A).

Investigations of the Ternary System $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ and Its Importance in the Production of Basic Bessemer Slags. G. Trömel. (Iron and Steel Institute, 1943, Translation Series, No. 147). This is an English translation of a paper which appeared in Stahl und Eisen, 1943, vol. 63, Jan. 14, pp. 21-30). (See Journ. I. and S.I., 1943, No. I., p. 157 A).

The Physical Chemistry of Open-Hearth Slags. J. White. (Iron and Steel Institute, 1943, this Journal, Section I). The principal oxides occurring in open-hearth slags are CaO , MgO , MnO , FeO , Fe_2O_3 , Al_2O_3 , P_2O_5 and SiO_2 , and a knowledge of the systems formed by these oxides with each other is essential to an understanding of the nature of the slag and of its rôle in steel-making. In the present paper the available data concerning these systems are discussed and correlated, thermal equilibrium and phase diagrams are given where these are available, and probable forms of

some of the as yet unknown diagrams are suggested on the basis of published information. Particular attention is paid to the equilibria governing the relationships between the oxides of iron and gaseous oxygen on the one hand, and between these oxides and metallic iron on the other. The modifying effects produced by the presence of other oxides on these relationships are also considered under the headings of the appropriate systems. Hence, the mechanism of gas oxidation in the furnace is briefly discussed.

On the basis of the data thus presented the question of the constitution of actual furnace slags is discussed, and a tentative scheme of phase assemblages in solidified basic slags is put forward, which, it is hoped, may serve as a basis (to be proved or amended) for further work on the subject. Fusibility and fluidity relationships in furnace slags are also considered in so far as they limit the range of "workable" compositions. Finally, the question of the molecular constitution of liquid slags is dealt with briefly.

FORGING, STAMPING AND DRAWING

(Continued from pp. 79 A-80 A)

Steel Cartridge Cases. R. B. Schenck. (Industrial Heating, 1943, vol. 10, May, pp. 639-660). **Production of 75 mm. Steel Cartridge Cases.** R. B. Schenck. (Iron Age, 1943, vol. 151, May 6, pp. 58-61). A brief illustrated description is given of the manufacture of 75-mm. steel cartridge cases at a plant of the General Motors Corporation. The following is a list of the major operations performed: Cut off blank, grind outside diameter, heat, extrude, redraw hot, size cold, anneal, pickle and rinse, coin head, bonderise, draw, trim end, first cold redraw, second and third cold redrawing, trim end, fourth cold redraw, bonderise, cold head, flame anneal, first and second tapering, flame anneal, machining the base, face to length, finish-ream and counterbore, inspect and repair, anneal, pickle, paint and bake.

Gadsden Feeds the 105's. W. N. Howley. (Machinist, 1943, vol. 87, July 3, pp. 101-116). The author gives a detailed description of the plant and processes for the mass production of 105-mm.-dia. shells at a new ordnance plant at Gadsden, Alabama. The raw material consists of 4 x 4-in. billets cut in 9-in. lengths. The hollow shell body is made in a Birdsboro piercing press and is subsequently machined and heat treated. Nearly all machining operations are done with tungsten-carbide-tipped tools.

The Effect of Back Pull when Drawing Steel Wire. W. Lueg and A. Pomp. (Mitteilung aus dem Kaiser-Wilhelm-Institut für Eisenforschung: Stahl und Eisen, 1943, vol. 63, Mar. 25, pp. 229-236). The authors report the results of tests in the drawing of patented

steel wire (carbon 0.58%) and a low carbon steel in which the back-pull technique was applied. The apparatus used enabled the forward pull, the back pull and the stress on the die to be measured. The data obtained were in agreement with the calculated results. In all the tests there was a large increase in the forward pull as the stress on the die was decreased and a smaller decrease in the work of drawing required to recover completely the work done in the backward pull. The decrease in the die stress is considerable and is at a maximum with the smallest reduction in diameter. On the other hand, the rate of increase of forward pull is greater with increasing back pull at small reductions than at large reductions in diameter. The temperature at the surface of the wire as it leaves the die decreases with increasing back pull; there is also a slight decrease in the wire diameter with increasing back pull. The decrease in the load on the die caused by applying back pull results in increased die life and permits higher drawing speeds to be used.

ROLLING-MILL PRACTICE

(Continued from pp. 81 A-82 A)

Rolling Heavy and Medium Plates. E. Howahr. (Blast Furnace and Steel Plant, 1943, vol. 31, Mar., pp. 309-315; Apr., pp. 419-422). An English translation is presented of a paper describing modern mill-stands and auxiliary machinery for rolling heavy and medium plates. This appeared originally in *Stahl und Eisen*, 1941, vol. 61, Jan. 23, pp. 73-83; Jan. 30, pp. 100-107. (See *Journ. I. and S.I.*, 1941, No. I., p. 211 A).

Increasing the Production of Section Mill Trains by Time Studies. K. Wuhrmann. (*Archiv für das Eisenhüttenwesen*, 1943, vol. 16, Mar., pp. 375-380). The author describes how a comprehensive time study was carried out at a mill rolling a variety of sections. The study, and the new wages agreement which was based on it, resulted in a substantial increase in production.

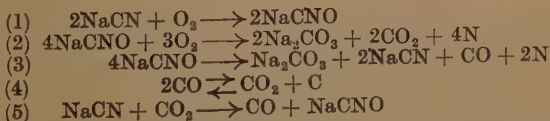
Making Hollow Steel Drills. E. N. Simons. (*Metals and Alloys*, 1943, vol. 17, Feb., pp. 320-325). The author describes British practice in making hollow drill steel. The best drill steel contains silicon 0.2%, sulphur plus phosphorus 0.04% max., manganese 0.4% max. and carbon in one of the three ranges 0.62-0.68%, 0.72-0.78% and 0.87-0.93%. Rolling on a mandrel and rolling on a sand core are now virtually obsolete processes. There are three up-to-date methods, *viz.*, rolling on a copper core, rolling on a metal core, and casting round a tube before rolling. In all the processes the rolling is carried out within the range 1100-700° C., with the last pass at as near 700° C. as possible to ensure a fine structure. In the first method a copper rod is inserted in a hole drilled down the centre of

the billet, which is then heated and rolled; the rod is afterwards extracted. As the copper offers little resistance to deformation during rolling, the hole in bars prepared in this way is frequently of irregular shape. The metal core process is the best of the three; in it a hole is drilled down the centre of the billet, and a core of special steel, having a higher coefficient of expansion than the drill steel, is inserted; the billet is heated up and rolled. After cooling, the bar is placed in a special machine with jaws which grip the rod and the end of the core; as the core steel has a high elongation (over 65%), it extends so much before fracture that the cross-sectional area is reduced and it becomes loose in the hole. In one of the Dominions the drill steel is cast in a mould which has a steel tube fixed down the centre; the ingot is rolled and the hole is formed by the tube which becomes welded into the drill steel. To prevent corrosion of the interior surface a method has been perfected by which a stainless-steel tube is inserted and fixed in the hollow drill steel.

HEAT TREATMENT

(Continued from pp. 82 A-85 A)

Liquid Nitriding. J. G. Morrison. (Iron Age, 1943, vol. 151, Apr. 15, pp. 41-45). The author discusses the liquid nitriding of tool steel by which process the hardness of hardened high-speed steel can be increased from Brinell 850 to 1100. A mixture of 60% of sodium cyanide with 40% by weight of potassium cyanide is used, and it must be aged for 12-16 hr. at 1050° F., as tools nitrided in fresh baths are brittle; this brittleness is probably due to the paucity of nascent nitrogen causing a steep nitrogen gradient at the surface of the steel. After ageing, the cyanate radical content is sufficiently high for the melting point of the bath to be 800° F. or lower. The usual bath temperature employed is 1050° F. The following five reactions occur, the first two at the surface of the salt exposed to the air and the other three at the surface of the steel which acts as a catalyst:



The most important reaction is (3), for this releases the nascent nitrogen for nitriding. Reaction (4) is an inhibiting one. With continued use, the cyanide of the bath decreases and the cyanate and carbonate increase. The bath must be replenished regularly with additions of 80% of sodium cyanide and 20% of potassium

cyanide. In cooling a thoroughly aged bath from about 1050° F. a "salting out" of carbonate occurs at about 925° F. By cooling to 875° F. most of the carbonate will fall to the bottom of the pot, whence it can be removed with a perforated ladle. A piece of high-speed steel immersed in a cyanide bath forms a galvanic cell. In a freshly prepared bath a peak potential of about 22 millivolts is registered after about 62 sec., and after 8 min. immersion a negative potential is registered. The case depth can be measured microscopically after etching the specimen in 4% nital. The maximum surface hardness is attained after immersion for 2-3 hr. at 1050° F.; increasing the time increases the case depth, but the surface hardness tends to decrease. The process can be applied to all classes of high-speed steel.

Nitriding Furnaces. (Automobile Engineer, 1943, vol. 33, July, pp. 277-282). Modern American practice in the design and application of nitriding furnaces is discussed. Details are given of continuous, semi-continuous and batch-type furnaces with actual production data for certain work. Methods of automatic temperature control for fuel-fired and electrically heated furnaces are also described. Reference is made to instruments for measuring ammonia flow and to the consumption of ammonia under normal commercial conditions.

A Study of the Processes Involved in the Malleablising of Unalloyed and Alloyed Malleable Cast Iron in Carbon-Monoxide/Carbon-Dioxide Mixtures. W. Baukloh, F. Schulte and H. Friederichs. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 341-354). The authors report on a laboratory investigation of the decarburising of white cast iron in CO-CO₂ mixtures at temperatures between 950° and 1050° C. The effect of wall thickness, annealing time and temperature, and gas composition, as well as that of the carbon content of the iron and the elements manganese, nickel, chromium, vanadium and sulphur, were studied. The conclusions were: (1) The rate of decarburisation increases with the temperature; in the first 2 hours the rate is many times that at the end of 10 hours. (2) The gasification of the carbon takes place almost entirely at the surface of the metal; to keep the reaction going, the carbon migrates from the interior to the surface, and the rate of diffusion determines the rate of decarburisation; this confirms Ledebur's theory for this reaction. (3) The rule that, with steel, the amount of carbon converted to gas in unit of time is proportional to the initial carbon content, cannot be applied to the hypo-eutectoid white irons. For short annealing times the precipitation of primary cementite, which increases with increasing carbon content, appears to lower the diffusion and decarburisation rates, whilst for long annealing times this phenomenon is scarcely noticeable. (4) Small additions of manganese, nickel, chromium and vanadium have but little effect on the rate of decarburisation; with higher percentages the effect is usually unfavourable, but molybdenum does increase

the rate at 1050° C. Sulphur appears to hinder the diffusion of carbon to the surface. (5) At low gas velocities the maximum rate of decarburisation occurs with a mixture of 28% of CO₂ with 72% of CO. (6) With CO₂ above about 28%, scaling occurs at 1050° C. and the decarburisation rate is lowered. (7) White iron can be decarburised without scaling by a CO₂-CO mixture of a composition in equilibrium with wüstite, provided that the carbon content is not below a critical amount; at carbon contents below this the CO₂ content of the mixture must be decreased to avoid scaling. (8) The results obtained with pure CO-CO₂ mixtures can be applied to decarburising-annealing with CO-CO₂ mixtures containing nitrogen provided that the CO/CO₂ ratio is favourable and the rate of gas flow is sufficiently high; care must be taken that the velocity of the decarburisation reaction at the surface is sufficiently rapid to satisfy the rate of carbon diffusion.

The Decarburisation of Cast Iron and Malleable Cast Iron in Hydrogen and in Mixtures of Hydrogen and Water Vapour. W. Baukloh and A. K. Foroud. (*Archiv für das Eisenhüttenwesen*, 1943, vol. 16, Mar., pp. 355-362). The authors report on an investigation of the decarburisation in hydrogen and in mixtures of hydrogen and water vapour of a pure iron-carbon alloy containing 3.96% of carbon, a grey iron, a malleable cast iron and three pure iron-carbon-manganese alloys containing up to 5% of manganese. The addition of about 2% by volume of water vapour to hydrogen markedly reduces the decarburising time required. The effect of a low manganese content on the decarburisation in hydrogen is very slight. 80% ferro-manganese cannot be decarburised in pure hydrogen. Calculations are presented which prove that, generally speaking, decarburisation in gases containing an oxidising agent is almost entirely dependent on the rate of diffusion of the carbon in the iron. When annealing at high temperatures in pure hydrogen the conditions are reversed; in this case it is the speed with which the hydrogen can react with the carbon that governs the rate of decarburisation.

A Study and Review of the Use of Copper in Selective Carburising. M. M. Thompson. (*Proceedings of the American Electroplaters' Society, Thirtieth Annual Convention*, June, 1942, pp. 28-33). After a review of the older literature on the use of copper for selective carburising, the author reports on his attempts to replace the standard cyanide bath by some acid and alkaline copper baths common in modern plating practice, especially by those used in the production of bright copper deposits. He found that the baths tried offered little advantage as compared with the standard cyanide bath, and that the greater thickness of the coatings obtained with the former was of value only because thicker coatings are less liable to be porous.

WELDING AND CUTTING

(Continued from pp. 85 A-86 A)

New Electrodes Expand Uses of Alternating-Current Arc Welding. H. Lawrence. (Steel, 1943, vol. 18, Apr. 19, pp. 98, 124-128). The author describes the development of electrodes for welding in all positions using alternating current. A.C. welding machines take less time to build than D.C. machines and there is less current loss with the former than the latter during idle time. In 1942 two makes of A.C. welding electrodes suitable for vertical and overhead welding became available in the United States in sizes up to $\frac{5}{32}$ in. in dia.; with these, weld metal with an elongation of at least 22% on 2 in. could be deposited.

Arc Welding Electrodes. H. O. Westendarp, jun. (Iron Age, 1943, vol. 151, Apr. 29, pp. 39-41; May 6, pp. 62-66). The author gives a brief description of the manufacture of welding electrodes and the technique of welding. The coating is applied to the full length of each wire by an extrusion press, after which a stripper brush removes from $\frac{5}{8}$ to $\frac{3}{4}$ in. of coating from one end. The electrodes are then dried, weighed, inspected and packed. There are three principal types of coating: (1) Cellulose-base coatings with a high ignition loss; this is a high-quality coating for all-position electrodes; (2) mineral coatings which are usually confined to electrodes for horizontal welding; and (3) rutile, or titanium oxide, coatings for all-position welding. The effects of changing the current setting, arc length, angle of electrode and speed of travel are discussed.

Comparable Arc Welding Electrodes. (Iron Age, 1943, vol. 151, May 13, pp. 72-78). Tables are presented showing the trade names and applications of welding electrodes of the leading American manufacturers to the classification numbers of the American Welding Society and of the American Iron and Steel Institute.

Behavior of Spot Welds under Fatigue Stress. A. M. Unger, H. A. Matis and E. P. Gruca. (Welding Journal, 1943, vol. 22, Mar., pp. 135-S-142-S). The author describes an investigation of the fatigue strength of spot welds in specimens of 18 gauge sheets of Cor-Ten steel (a low-alloy chromium-copper-silicon steel) and cold-rolled 18/8 stainless steel. A standard Krouse fatigue-testing machine for sheet metal was used. With an electrode pressure of 1200 lb. and passing 12 cycles of current through the Cor-Ten and 10 cycles through the stainless steel, the fatigue strength in both cases increased with increasing welding current up to a critical value, but on increasing the current still further the fatigue strength decreased.

Welding of 4 to 6% Chromium Molybdenum Titanium Steel. E. H. Wyche. (Welding Journal, 1943, vol. 22, Mar., pp. 142-S-144-S). The author reports the results of tests to ascertain by

hardness surveys which of four types of electrodes was best for welding chromium-molybdenum-titanium steel containing 4-6% of chromium. The electrodes used contained: (1) Chromium 4-6% plus molybdenum; (2) chromium 4-6% plus molybdenum and columbium; (3) chromium 18%, nickel 8% plus columbium; and (4) chromium 18%, nickel 8% plus titanium. The third type produced the best weld with only a very slight amount of hardening resulting from dilution of the weld metal by the base metal.

Two Methods of Brazing High Speed Steel Tips. B. S. Lement and W. B. Kennedy. (Iron Age, 1942, vol. 150, Nov. 19, pp. 55-58). Two methods of fixing molybdenum high-speed steel tips to carbon steel shanks are described. In the first, after cleaning the parts, the shank is covered with flux and pushed into a small electric furnace to melt and spread the flux. The tip and shank are then fitted together, with a thin strip of copper in between. The tool is then preheated to 1500° F. before heating to 2225° F., from which temperature it is quenched in oil to below 200° F. The second method is by silver soldering.

CLEANING AND PICKLING OF METALS

(Continued from pp. 24 A- 25A)

Polishing Steel Specimens Prior to Plating for Exposure Tests. G. A. Lux. (Proceedings of the American Electroplaters' Society, Twenty-Ninth Annual Convention, June, 1941, pp. 54-61). This is a preliminary report on an investigation—sponsored by the American Electroplaters' Society and the Bureau of Standards—on the effect of the mode of polishing the base metal on the protective value of electrolytic nickel and chromium coatings. The report is confined to the study of the polishing of steel specimens with flexible wheels with abrasive grains glued to their surface, the results obtained being listed in several tables. The polishing equipment used as well as the methods applied to the examination of the surface finish are described at some length.

Polishing with Glue-Abrasive Mixtures. J. F. Siefen. (Iron Age, 1943, vol. 151, Mar. 18, pp. 56-57). The author gives some information on a proprietary brand of abrasive compound used for obtaining a polished surface on highly stressed engine parts so as to prevent fatigue failures. The compound is a cold glue with a sodium silicate base and it contains abrasive grains. It can be brushed on the polishing wheel and it sets within 8 min. The wheel can be reconditioned by applying another coat when necessary.

Contamination and Cleaning of Cold Rolled Steel. E. H. Lyons. (Proceedings of the American Electroplaters' Society, Twenty-Ninth Annual Convention, June, 1941, pp. 118-122). The author

discusses the cold-rolling of steel in an elementary way, with especial reference to the use of various oils and greases as cooling agents and their subsequent removal.

COATING OF METALS

(Continued from pp. 25 A-30 A)

Laws Governing the Growth of Films on Metals. U. R. Evans. (Electrochemical Society, 1943, Preprint No. 83-10). The author discusses the following three growth laws which express the rates of formation of films on metal surfaces :

$$\begin{aligned} y &= k_1 t && \text{(linear law)} \\ y^2 &= k_2 t + k_3 && \text{(parabolic law)} \\ y &= k_4 \log (k_5 t + k_6) && \text{(logarithmic law)} \end{aligned}$$

where y is the thickness of the film, t is time and k_1, k_2, k_3, k_4, k_5 and k_6 are constant at any given temperature. The linear law occurs with the porous films formed on light metals which allow inward leakage of oxygen or other non-metal. The parabolic law occurs with non-porous films possessing ionic and electronic conductivity, and is governed by outward ionic migration under a potential gradient; it is usually associated with vacant sites in the cationic lattice. The logarithmic law occurs when the conditions needed for parabolic thickening are absent, and is believed to be due to the outward passage of interstitial matter through flow-paths or zones of loose structure in the outer part of the oxide film; the actual rate of passage along a given path is regulated by the rate of crossing a less pervious inner film of constant thickness and is independent of the thickness of the outer film, provided that no obstruction occurs in the path through the outer film. If such an obstruction occurs, passage along the path in question becomes impossible, and clearly the chance of obstruction of a given path will increase with the film thickness. The growth rate falls off with film thickness in accordance with the logarithmic law.

Protective Chemical and Surface Finishes for Scientific Instruments and Apparatus. H. Sutton. (Symposium on Protective Finishes for Scientific Instruments and Apparatus: Journal of Scientific Instruments, 1943, vol. 20, June, pp. 86-92). The author describes means of protecting the metal surfaces of instrument parts against corrosion. Stainless-steel screws tend to seize when tightened up in other parts also made of stainless steel; this can be overcome by heating the pieces in air or in a mixed nitrate salt bath until the surface becomes coated with a thin, pale brown film of oxide. A very effective method of descaling steel is one due to Tainton, in which the pieces are made the cathode in a bath containing molten sodium hydroxide and sodium carbonate as electrolyte. The

Granodine process, Parkerising and Walterisation are all phosphatising processes. The natural colour of phosphate-treated steel is grey. Good black finishes are obtained by impregnation of the coating with black dyes followed by greasing or oiling. Cadmium-plated surfaces are not ideal for paint or varnish coatings, but they can be made suitable by immersion for a few minutes in an aqueous solution containing about 1% of chromic acid and about 0.1% of sulphuric acid; this produces an oxide film to which paint will adhere exceedingly well. Cadmium-plated parts used in enclosed spaces in which electrical gear is housed sometimes develop a thick white incrustation; this is due to the presence of vapours (*e.g.*, acetic acid) liberated by certain plastics and insulating materials. Electro-tin deposits 0.0003–0.001 in. thick are used on the steel parts of instruments that have to be soldered, especially when it is desired to use a non-corrosive flux.

Protective Paints and Varnishes for Scientific Instruments and Apparatus. W. E. Wornum. (Symposium on Protective Finishes for Scientific Instruments and Apparatus: *Journal of Scientific Instruments*, 1943, vol. 20, June, pp. 98–102). The author presents a survey of means of preparing metal surfaces and of the application and properties of paints and varnishes. After a film has been applied and levelling-out has taken place, but before solid film formation sets in, most of the solvents will have evaporated. Changes in surface tension can then occur in that the film, instead of remaining evenly spread, may recede into drops, or contract away from any sharp edges or from specks on the surface, the latter being a special case of pin-holing. This defect is commonly called "cissing," and it indicates poor wetting conditions. Cissing is prone to occur with stoving finishes. A finish applied to identical sheets of the same metal may ciss badly on stoving but not on air-drying. There is some connection between cissing and adhesion, for those finishes which ciss on stoving usually produce films with poor adhesion when air-dried on similarly prepared surfaces. Finishes can usually be obtained to meet any particular requirements, but the adhesion and strength of the coating may be seriously impaired if the proper stoving conditions are not maintained. Under-stoving will affect the hardness and drying of the film. The introduction of infra-red stoving has reduced the stoving time for suitable coatings from the 30 min. to 2 hr. necessary in the box to 4–6 min. under the lamps. Synthetic resin media may be divided into two main types, the reversible and the irreversible in respect to their behaviour towards solvents when they have dried out as films. The spirit varnishes and cellulose lacquers belong to the former. The latter group may be sub-divided into the element convertible and the heat convertible. By the addition of oxygen to the element-convertible media, as in the drying process, they are converted into the insoluble form as films. The heat-convertible media are characterised by the fact that resinification proceeds at the stoving temperature producing

irreversible films; they are mainly represented by the urea-formaldehyde resins.

Hard Chromium Plating and Some of Its Practical Applications. H. M. Dean. (Australian Institute of Metals: Australasian Engineer, 1943, vol. 43, Jan. 7, pp. 13-14). The author describes the equipment and process employed for hard chromium plating at the works of Metal Manufacturers, Ltd., Port Kembla. Using a current density of $1\frac{1}{4}$ amp. per sq. in. of surface, the rate of growth of plate is about 0.0005 in. per hr. In the bath, which is held at 113° F., the $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio is maintained at 100 and the specific gravity of the solution at 1.2. Annealing chromium plate at 300° C. for 30 min. removes any hydrogen which may have been absorbed during the plating, and in some cases it removes the brittleness and improves the service life.

Hard-Chromium Plating. A. J. T. Eyles. (Mechanical World, 1943, vol. 113, Apr. 30, pp. 459-463). The author gives a brief outline of recent applications of hard-chromium plating and describes the process and equipment necessary. Details are given of specially designed anodes and brackets for plating the inner and outer surfaces of hollow cylindrical parts.

Preparation of Surfaces for Hard Chromium Plating. A. W. Logozzo. (Proceedings of the American Electroplaters' Society, Thirtieth Annual Convention, June, 1942, pp. 33-37). The author stresses the need of proper treatment of the steel before hard-chromium-plating, dealing briefly with the heat treatment, cleaning and pickling, and with the elimination of hydrogen to avoid embrittlement.

Electro-Deposited Rust Proofing Coatings. H. Silman. (Electro-depositors' Technical Society: Metallurgia, 1943, vol. 27, Apr., pp. 247-248; Automobile Engineer, 1943, vol. 33, May, pp. 195-198). The author discusses the relative values and purposes of electroplated coatings on steel. Copper is often applied as an undercoat to nickel, but, generally, thin copper deposits add little to the protective value of the nickel top-coat. There is some evidence that the protective value of a triple coating (nickel-copper-nickel) is greater than that of a nickel coat of equal thickness.

Nickel Plating Fine Wire. J. H. Conolly. (Iron Age, 1943, vol. 151, Apr. 1, pp. 50-51). The author gives a brief illustrated description of a continuous nickel-plating installation for the plating of the fine wire used to make filament supports in electric lamps.

Zinc Losses in Hot-Dip Galvanizing. W. G. Imhoff. (Metal Finishing, 1942, vol. 40, Nov., pp. 587-590). The author examines the theory that the zinc loss in hot-dip galvanising is due to evaporation. The results of tests are reported in which very careful weighings were made of the kettle, zinc, fluxes and steel sheet before galvanising and of the kettle, zinc, skimmings, dross and all possible sources of zinc consumption in the process. These tests were repeated at six galvanising temperatures in the $800-880^{\circ}$ F. range

and from the data obtained a "zinc balance" was set up. In all cases the differences between the zinc supplied and the zinc accounted for were so small in proportion to the total zinc that all of it could be considered as accounted for and that there was therefore no loss by evaporation.

Electrolytic Tinning. W. Cooper. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 31-34). The author describes a modern continuous electrolytic tinning plant for tinning strip up to 36 in. wide. The pickling tank is rubber-lined, and measures 51 in. wide, 12 ft. long and 11 ft. 6 in. deep. It has a series of rubber-covered rolls at the top and bottom over which the strip passes; these are closely spaced so that 190 ft. of strip are immersed. The strip then passes through wringer rolls and a cold rinsing tank into the plating bath, which is 50 ft. long and 10 ft. deep. The tank holds 15,000 gal. of electrolyte consisting of sodium stannate, sodium hydroxide and sodium acetate. In the tank the strip passes up and down in 48 vertical strands over two series of rolls. Tin anodes are suspended between the strands, and groups of eight anodes are each connected to a 10,000-amp., 8-V. generator. The strip is pulled through the entire line by a set of pinch-rolls. The amount of tin deposited is controlled by the speed of the strip, provided other conditions remain constant; at 350 ft. per min., 0.5 lb. of tin per basis box is deposited using 60,000 amp. at 8 V.

Electric Fusion of Tinplate. G. E. Stoltz, J. A. Hutcheson and R. M. Baker. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 49-55). The authors discuss the advantages and disadvantages of two electrical methods of reflowing tin coatings on steel strip. In the conduction method the heating current passes along the strip, contact being made through conductor rolls with pinch-rolls bearing on the other side of the strip to prevent burning and mechanical slip between the strip and the conductor rolls. With the induction method the first cost of the equipment is very high and the overall efficiency from the power line to the strip is 45%. The heating is accomplished by passing the strip through a high-frequency field of magnetic flux; there is no problem with regard to collecting the current through the tin coating, and the heating is uniform even if there should be a variation in gauge along the length of the strip. The requirements of the transformers, oscillators and rectifiers for the induction heating process are outlined.

High Frequency Heating Conserves Critical Tin. G. E. Stoltz. (Industrial Heating, 1943, vol. 10, Jan., pp. 92-95, 110). The author describes how high-frequency induction heating is applied in a tinplate mill to melt the tin while the strip is moving, and thus enable a thinner coat, very uniform in thickness, to be obtained (see preceding abstract).

New Applications of Electric Equipment for Electro-Tinning Lines. J. H. Hopper. (Blast Furnace and Steel Plant, 1943, vol. 31, Apr., pp. 423-427, 449, 450). **Electrical Equipment for Con-**

tinuous Electrolytic Tinplating. J. H. Hopper. (Iron and Steel Engineer, 1943, vol. 20, Mar., pp. 36-47). The author discusses the electric power requirements, circuits and methods of control for modern high-speed continuous electrolytic tinning plants.

Radio Tubes for Heat Treating by High-Frequency Induction. H. C. Humphrey. (Steel, 1943, vol. 112, Feb. 1, pp. 111-112). The author gives some particulars of the electrical circuits and equipment for supplying high-frequency current to inductor coils for heating and flowing tin on the surface of moving tinplate strip.

Applications of Phosphate Rust-Proofing in the War Program. V. M. Darsey. (Proceedings of the American Electroplaters' Society, Thirtieth Annual Convention, June, 1942, pp. 58-61). The author briefly describes the various phosphatising processes and outlines their application in wartime, with special reference to the production of "Steelbond" sheet and of black plate for the canning industry.

Protective Finish. (Steel, 1943, vol. 112, Feb. 22, pp. 106-109). Some particulars are given of a means of protecting finished steel parts from corrosion. The solution used is called "Phytanium-blended Pentrate." After cleaning in a hot alkali solution and rinsing, the parts are passed through two tanks of the proprietary solution, one at 285° F. and the second at 310° F. It is claimed that the liquid penetrates 0.00035-0.00045 in. and that the effect of any previous heat treatment is not impaired. Steel protected in this way has the ability to retain lubricating oil.

Electrodepositing Paint Spray. H. Ransburg. (Proceedings of the American Electroplaters' Society, Thirtieth Annual Convention, June, 1942, pp. 62-65). The author describes a new method of paint spraying, in which the article to be coated is surrounded by an electric field and earthed, so as to attract the sprayed particles.

PROPERTIES AND TESTS

(Continued from pp. 88 A-94 A)

The Effect of Carbide-Forming Elements on the Yield Point of Steel at Room Temperature. K. Dies. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 333-339). The author reports on an investigation of the effects of the carbide-forming elements titanium, vanadium, chromium and molybdenum on the "knee" in the stress-strain curve in steels containing 0.03-0.37% of carbon heat-treated in various ways. After normalising from 930° C. the knee disappears with the change of the cementite to special carbides. In the chromium and molybdenum steels the transition from elastic to plastic flow is a slow one; in the titanium and vanadium steels it occurs suddenly. The curves for air-cooled and furnace-cooled

titanium steels are similar in shape. With the vanadium steels, even after complete conversion of the carbide, the stress-strain curves are discontinuous for a certain range of vanadium contents, which indicates that vanadium carbide, under certain conditions, can, like iron carbide, cause a definite yield point to appear. Results with tempered specimens indicate that the existence of a yield point depends more on the distribution of the carbides than on their chemical nature. With the vanadium steels there is a critical distribution of the carbide particles which causes a definite yield point to appear.

Small Notched-Bar Specimens for Determining the Notched-Bar Impact Strength. A. Thum and R. Z. v. Manteuffel. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 367-374). The authors present and discuss the results of impact tests on small specimens measuring $27 \times 4 \times 3$ mm. with a 60° notch 1 mm. deep and a radius of 0.1 mm. The results with this size of specimen are comparable and reproducible, and the impact strength values obtained do not show too much scatter.

A Photoelastic Study of Stresses in Gear Tooth Fillets. T. J. Dolan and E. L. Broghamer. (Illinois University, Engineering Experiment Station, 1942, Bulletin Series No. 335). The authors report the results of tests undertaken to determine the maximum tensile stresses developed in the fillets of several representative types of gear-teeth by employing Bakelite models and the photo-elastic method of stress analysis. The conclusions reached were: (a) As the height of the load position was increased, the maximum fillet stress increased, but the stress concentration factors decreased; (b) the maximum fillet stresses increased rapidly as the fillet radius was reduced; (c) a definite decrease in the tensile-stress concentration factor was observed as the tooth model was gradually tapered inward to approach Lewis' ideal shape of a parabola of uniform strength, whereas no change in the compressive stress concentration factor occurred as the angle was varied over a range of 25° ; (d) no appreciable change in maximum fillet stress was produced by varying the angle between the bottom land of tooth-space and the thickness chord over a range of 15° ; and (e) generated fillets having the outline of an epitrochoid produced smaller localised stresses than circular fillets whose radius was equal to the minimum radius of the epitrochoid.

Hardness vs. Wear Resistance. J. R. Spence. (Welding Journal, 1943, vol. 22, Mar., pp. 179-181). The author shows that although the wear resistance of alloy steels increases with their hardness, this does not necessarily apply to hard-facing alloys deposited by means of welding electrodes. It is much more difficult to grind a hard-facing alloy than a heat-treated alloy steel, although the hardness of the two materials may be the same. A rough estimate of the wearing properties of hard-facing alloys can be obtained by making comparative grinding tests on them.

End-Quench Test for Hardenability and Its Application. W. E. Jominy. (Steel, 1943, vol. 112, Jan. 25, pp. 84-85). The author discusses the S.A.E. and A.S.T.M. methods of making and recording the results of end-quench tests, and their significance. The effect of carbon on the hardenability is relatively small, whilst its effect on hardness is relatively great. Steels which have approximately the same hardenability curves, but different carbon contents, do not have the same structures, and they cannot be substituted indiscriminately. Although two steels may have the same hardenability, it does not follow that they have the same machinability, impact strength and wear resistance; they probably have the same tendency to distort, but this has not been established.

The Embrittlement of Ingot Iron and Low-Carbon Steels. B. Jones. (Metallurgia, 1943, vol. 28, May, pp. 13-19). The mechanical properties of ingot irons, apart from the limit of proportionality, are remarkably constant and are practically unaffected by either the mass or the temperature of quenching from 650 to 1000° C. The hardness increases on quenching from temperatures up to 760° C., but is then constant, or actually falls until 900° C. is reached. The notched-bar impact value is remarkably low after quenching from 875° and 900° C., particularly in small sections. The embrittlement is not due to the presence of the relatively high carbon martensite areas, but to the larger areas of low-carbon martensite formed from the austenite that have increased in volume by spreading along the grain boundaries as the A_{c_3} point was approached. In the quenching of mild steel the brittle condition is found on quenching from temperatures close to the A_{c_1} point, and it coincides with the presence of martensite grains at the ferrite grain boundaries. Above the A_{c_1} temperature the austenite absorbs the adjacent ferrite grains and becomes lower in carbon content; on quenching, it forms a brown-etching type of dilute martensite. Quenching from 800° and 825° C. imparts a dog-tooth pattern to the martensite, which is also associated with low impact values.

An Iron-Silicon Alloy of High Initial Permeability Due to Special Metallurgical Treatment. F. Pawlek. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 363-366). The author reports the results of tests with various forms of heat treatment on a very pure 3%-silicon steel, the object being to produce the highest possible initial magnetic permeability. Increasing the temperature had a favourable effect when annealing in hydrogen contaminated by small quantities of nitrogen. Increasing the nitrogen and carbon reduced the initial permeability considerably. The highest initial permeability was obtained by annealing in pure hydrogen or in a vacuum. A pretreatment under oxidising conditions before annealing in a vacuum was very effective in producing a high initial permeability. Tests on commercial qualities of iron-silicon alloys yielded similar results; in particular it was seen that, with vacuum annealing, steel with initial permeability values equivalent to that

of alloys containing about 40% of nickel could be obtained. Plant for the full-scale utilisation of this process is now under construction.

Compacted Magnets with a Synthetic Resin Binder. H. Dehler. (Iron and Steel Institute, 1943, Translation Series, No. 149). This is an English translation of a paper which appeared in *Stahl und Eisen*, 1942, vol. 62, Nov. 19, pp. 983-986. (See Journ. I. and S.I., 1943, No. I., p. 179 A).

Creep Resistance of Superheater Tube Steels in Tube and Bar Form. J. A. Jones and W. E. Bardgett. (Engineer, 1943, vol. 176, July 2, pp. 6-8). The authors present the results of creep tests on two superheater tube steels, the object being to see whether creep-test data on bar material are representative of tube material of the same steel. A chromium-molybdenum steel with 0.60-1.20% of chromium and 0.40-0.80% of molybdenum, and a 0.50%-molybdenum steel were used. The tests were carried out at 1000° F. at stresses ranging from 5 to 11 tons per sq. in. for periods up to 48 days. The stresses giving creep rates of 10^{-6} in. and 10^{-7} in. per in. per hr. were 10.1 and 5.1 tons per sq. in. respectively for specimens cut from tubes, and 8.0 and 4.6 tons per sq. in. respectively for specimens from the bar material. A specimen was prepared from the bar having the same dimensions as the tube specimen. This was tested at 7 tons per sq. in., and the results showed that there was no size effect in the tests. Provided the tubes are produced by a satisfactory method and heat-treated under properly controlled conditions, the application of results of creep tests on bar material to tube design introduces a factor of safety of 25% in the case of the chromium-molybdenum steel for a creep rate of 10^{-7} in. per in. per hr. The creep-stress figure for the 0.5% molybdenum steel in bar form may be taken as directly applicable to the corresponding tube material.

Steels for Use at Low Temperature and Their Testing. H. J. Wiester. (Iron and Steel Institute, 1943, Translation Series, No. 146). This is an English translation of a paper published in *Stahl und Eisen*, 1943, vol. 63, Jan. 21, pp. 41-47; Jan. 28, pp. 64-74. (See Journ. I. and S.I., 1943, No. I., p. 180 A).

Plain Carbon Replaces Alloy Steels. Q. S. Jameson. (Iron Age, 1943, vol. 151, May 6, pp. 47-56; May 13, pp. 59-65). The author compares the properties, in particular the hardenability, of low-carbon steels and low-alloy steels and shows that A.I.S.I. (American Iron and Steel Institute) steel C 1022 containing carbon 0.22% and manganese 0.70-1.00%, quenched in water instead of oil, can be used for many applications in place of low-alloy steels.

Austenitic Manganese Steel. L. P. Young and D. H. Goard. (American Society for Metals: Canadian Mining and Metallurgical Bulletin, 1943, Apr., pp. 170-174). The authors briefly review the methods of making austenitic manganese steel and its properties.

Boron. T. W. Lippert. (Iron Age, 1942, vol. 150, Nov. 19, pp. 41-44). The author discusses methods of adding boron to steel and

its effects. The addition of 0.002% of boron is equivalent to 0.35% of chromium or 0.25% of molybdenum as far as increasing the hardenability is concerned. Its effect on low-carbon steel is often excessive, and the addition is therefore only recommended for steels in the 0.20–0.60% carbon range. A number of proprietary compounds containing boron are available in addition to two grades of ferro-boron containing 15–20% and 10–12% of boron respectively.

User Report No. 9 on Experience with NE (National Emergency) Alloy Steels. A. S. Jameson. (Steel, 1943, vol. 112, Feb. 1, pp. 100–106, 134). Data are presented on the properties, particularly the hardenability, of the NE 9400 and NE 9600 series of steels.

Significant Steels Commonly Used for Specific Articles. (Iron Age, 1942, vol. 150, Nov. 19, pp. 51–54). A list prepared by the American Iron and Steel Institute is presented in which articles made of steel are placed in alphabetical order, and opposite each is given the S.A.E. or A.I.S.I. specification number for the steel. The list is intended to facilitate the sorting of scrap according to analysis.

Aeronautical Material Specifications. (Iron Age, 1943, vol. 151, Apr. 29, pp. 47–53). Seven pages of tables are presented which show in condensed form the composition and some of the properties and applications of the American A.M.S. steels (Aeronautical Material Specification).

Shell Metallurgy Specifications. H. H. Zornig. (Society of Automotive Engineers: Heat Treating and Forging, 1943, vol. 29, Mar., pp. 134, 147; Apr., pp. 183–184, 204). The author discusses American Army Ordnance specifications for steels for shells. Fragmentation shells can be made of 0.10–0.20% carbon steel containing 1.00–1.30% of manganese without heat treatment. For shells larger than 40 mm. the carbon content may be up to 0.65%, the manganese 1.00% max., phosphorus up to 0.55%, silicon 0.15–0.35% and sulphur up to 0.055%.

Addendum to Second Report of the Research Committee on High-Duty Cast Irons for General Engineering Purposes. J. G. Pearce. (Proceedings of the Institution of Mechanical Engineers, 1943, vol. 149, No. 3, pp. 101–102). This addendum to the Second Report (see Journ. I. and S.I., 1941, No. II., p. 184 A) of the Research Committee of the Institution of Mechanical Engineers deals with the extent to which phosphorus can be used in alloyed or specially processed cast irons required to meet the highest specifications for mechanical tests. For alloyed irons with properties equal to those of grade 2 irons in British Standard Specification No. 786, the tensile and transverse strengths and transverse deflection increase as phosphorus increases up to about 0.35%; with a further increase in phosphorus they decrease uniformly. For the higher-strength irons equal to Grades 3 and 4 of the above specification the rise in static properties up to 0.3% of phosphorus has not been observed, except in individual cases. The Brinell hardness number increases uni-

formly with the phosphorus, and a rise of 3 points for each 0.1% of phosphorus may be expected as compared with a non-phosphoric iron.

Third Report of the Research Committee on High-Duty Cast Irons for General Engineering Purposes. J. G. Pearce. (Proceedings of the Institution of Mechanical Engineers, 1943, vol. 149, No. 3, pp. 103-112). The Third Report of the Research Committee of the Institution of Mechanical Engineers is in two parts. Part 1 contains results of further tests on commercially made high-duty cast iron, *i.e.*, irons with properties equal to, or better than, those of grade 2 iron in British Standard Specification No. 786. In Part 2 the results of the remainder of the experimental programme concerning alloy cast irons, showing the influence of nickel, copper, chromium and molybdenum on certain selected compositions are reported.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 94 A-96 A)

Metallurgical Terminology. A. F. Dunbar. (Australian Institute of Metals: Australasian Engineer, 1943, vol. 43, Apr. 7, pp. 14-15, 45-51). The author discusses the difficulties which arise owing to the growth of unsystematised nomenclature in metallurgy. At a training centre for metallurgists in Melbourne it has been found best to teach the student the fundamental difference in formation and habit between the primary and secondary products of austenite. Only after this is fully grasped are the common, and in many cases misleading, names in current use mentioned, and then only so that the student may recognise them in the literature. In other words, a simple systematic classification of the observed microstructures replaces the heterogeneous collection of names which has grown up through tradition. Thus, the primary products are referred to as coarsely laminated pearlite, finely laminated pearlite, nodular pearlite and acicular pearlite. Similarly, the secondary structures obtained on tempering are all classified as granular pearlite of different states of aggregation from fine to coarse. The naming of alloys and ambiguous terms in heat treatment and other processes are discussed.

The Electrolytic Polishing of Stainless Steels. H. H. Uhlig. (Proceedings of the American Electroplaters' Society, Twenty-Ninth Annual Convention, June, 1941, pp. 20-24). The author describes the use of glycerine/phosphoric-acid mixtures for the electrolytic polishing of 18/8 steel. The quality of the polish produced was studied with the aid of a photo-electric spectrophotometer. The best results were obtained with an electrolyte consisting of approximately 42% of orthophosphoric acid, 47% of glycerine and 11% of water,

used at 100° C. or higher with an anodic c.d. of at least 0.1 amp. per sq. in. For practical purposes the glycerine can be replaced by other organic substances with one or more hydroxyl groups. The mixtures of phosphoric acid with organic substances are suitable also for the polishing of other alloy steels and of mild steel. The polish obtained is not quite so satisfactory, however, as on 18/8 steel. In conclusion the theoretical reasons for the organic addition are discussed.

Electropolishing Stainless Steel in Phosphoric-Sulfuric Acid Baths.

C. L. Faust and H. A. Pray. (Proceedings of the American Electroplaters' Society, Twenty-Ninth Annual Convention, June, 1941, pp. 104-112). The authors report on an extensive study of the electrolytic polishing of 18/8 and other chromium-nickel and chromium steels with a view to a wider application of this method in industrial finishing practice. They used sulphuric-acid/phosphoric-acid baths in a great variety of proportions, with an admixture of up to 20% of chromium trioxide, and studied the effect on the surfaces obtained of the voltage, the current density, the temperature, the original surface condition and of various modes of stirring the baths. The results are presented in extensive tables and several diagrams. Data are also given regarding the life of the baths and the equipment required.

Electrolytic Polishing of Metals. S. Wernick. (Society of Chemical Industry and the Electrodepositors' Technical Society, Joint Meeting: Chemistry and Industry, 1943, vol. 62, June 26, pp. 238-241). The author discusses the development, and present position of the electrolytic polishing process with special reference to stainless steel. Phosphoric-acid-based electrolytes consistently produce a polish superior to that obtained with electrolytes based on sulphuric acid, but the current requirements with the latter are less exacting. Foreign bodies and local inclusions in the surface of stainless steel are likely to be accentuated by the electropolishing action. Optimum results cannot be obtained on all stainless steels from the same electrolyte. Some initial mechanical polishing treatment is usually required. Plain flat surfaces are the most difficult to treat.

Optical Cut Method for the Determination of Surface Roughness.

J. F. Kayser. (Foundry Trade Journal, 1943, vol. 70, June 17, pp. 137-138). The author describes an optical method of obtaining a profile curve of a metal surface, or, more briefly, an optical cut. The apparatus used, which is described and illustrated, is a Vickers projection microscope, with a suitable addition to the illuminating system and a subsidiary stage to hold the sample to be examined. The illuminating system is so arranged that it is possible to focus the image of a straight edge on to the surface under examination. The straight edge is provided by a stainless-steel safety-razor blade.

Electronic Energy Bands in Body-Centered Iron. M. F. Manning. (Physical Review, 1943, vol. 63, Mar. 1 and 15, pp. 190-202).

Calculations of the electronic energy bands in body-centred iron by the Wigner-Seitz-Slater method are reported. There are found to be two filled and four partially filled bands. The lowest two bands are responsible for the cohesion; the next three partially filled bands for the ferro-magnetism; the highest band is responsible for the electrical conduction. The density of states is calculated as a function of the energy and compared with similar results obtained by Greene for face-centred iron. The higher density of states in body-centred iron accounts for the fact that it is ferro-magnetic, whilst face-centred iron is not. It also indicates a greater electronic specific heat for body-centred iron than for face-centred iron. This higher electronic specific heat is responsible for the high temperature change from a face-centred to a body-centred structure.

Electronic Energy Bands in Face-Centered Iron. J. B. Greene and M. F. Manning. (Physical Review, 1943, vol. 63, Mar. 1 and 15, pp. 203-210). Calculations of the electronic energy bands for face-centred iron by the Wigner-Seitz-Slater method are reported. There are found to be two filled and four partially filled bands. The density of states is calculated as a function of the energy; the density-of-states/energy curves appear to be quite similar to those calculated by Slater for copper, but resemble more closely those for body-centred iron.

The calculated electronic specific heat is found to agree fairly well with the difference from $3R$ of the experimentally measured specific heat. There are no experimental data for the specific heat of face-centred iron at low temperatures.

The Metallurgy of Modern Alloys. R. H. Harrington. (Heat Treating and Forging, 1942, vol. 28, Sept., pp. 468-471, 488, 489; Oct., pp. 528-531; Dec., pp. 627-630; 1943, vol. 29, Mar., pp. 132-133, 148; Apr., pp. 179-182, 206). In Part I. of this series of articles the author explains heat-treatment processes by reference to the iron-carbon diagram and proposes that heat-treatment definitions should be considered in three groups related respectively to (a) allotropic modifications, as in the iron-carbon system, (b) the cold-worked solid solutions exemplified by cold-rolled brasses, and (c) precipitation-hardening alloys with the now popular copper-beryllium as an example. In Part II. the classification of general types of equilibrium diagrams, the construction of these diagrams and their application to predict the behaviour of various alloy compositions on solidification and after heat treatment are considered.

Constitution of the Iron-Rich Iron-Nickel-Silicon Alloys at 600° C. E. S. Greiner and E. R. Jette. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1573: Metals Technology, 1943, vol. 10, Apr.). The authors report the results of an X-ray investigation of the iron-nickel-silicon system at 600° C. using specially prepared alloys with composition in the range iron 56-90.3%, nickel 2.3%-34.4% and silicon 2.4%-32.9%. The

body-centred cubic phase in the ternary diagram is bounded by four two-phase areas. Three three-phase areas separate the respective two-phase areas. Three of the phases in these polyphase areas have the same structures as corresponding phases in the binary iron-nickel or iron-silicon alloys. In addition, two new phases, the structures of which were tentatively identified, were observed. The solid solubility limit of the α -phase at 600° C. was determined from lattice-constant data. The solubility of nickel in the α -phase changes from 3.5 atomic-% in the binary iron-nickel alloys to 13.6 atomic-% in the ternary alloys containing 22.4 atomic-% of silicon. From the latter composition, the solubility of nickel in the α -phase changes to 7.9 atomic-% at 26.8 atomic-% of silicon, and is of course zero at 26.4 atomic-% of silicon in the binary iron-silicon alloys.

The Brittle Constituent of the Iron-Chromium System (Sigma Phase). I.—A Survey of the Limits of the Sigma Phase in the Binary System. A. J. Cook and F. W. Jones. (Iron and Steel Institute, 1943, this Journal, Section I). The existence of a second phase in the binary iron-chromium system has been confirmed and the phase boundaries have been established down to a temperature of 600° C. X-ray powder photographs have been used to identify the phases after annealing filings and solid samples at various temperatures. A marked feature of the phase is a very slow rate of reaction near its upper temperature limits, which it is considered is due to true hysteresis. The presence of cold-work has been found to have an accelerating effect on the rate at which the σ constituent can be produced in the alloys. Microphotographs are shown of partial and complete transformation from the α to the σ phase.

CORROSION OF IRON AND STEEL

(Continued from pp. 57 A–59 A)

Present Position of the Corrosion Committee's Field Tests on Atmospheric Corrosion (Unpainted Specimens). J. C. Hudson. (Iron and Steel Institute, 1943, this Journal, Section I). This paper brings up to date the information given in earlier Reports of the Corrosion Committee concerning atmospheric corrosion tests made on ordinary ferrous materials of construction, including wrought irons, ingot irons and steels both of ordinary and of the low-alloy type. The main tests were made at fourteen stations, seven at home and seven overseas, representing marine, rural, industrial, tropical and arctic conditions. The specimens measured $15 \times 10 \times \frac{3}{8}$ in., and were exposed vertically.

Comparison of the corrosive effects of different atmospheres indicates that the primary cause of serious corrosion of ferrous materials is pollution of the air with sulphur gases. The maximum

rate of corrosion observed for ordinary mild steel over a five years' period was 0.0042 in. per year in the industrial atmosphere of Sheffield. Much lower rates were recorded at most overseas stations. The corrosion rate probably decreases with increasing time of exposure. Wrought irons containing much slag are more resistant to atmospheric corrosion than mild steel, but those with low slag contents are more corrodible. Ingot iron resists general corrosion to much the same extent as mild steel, but Aston-Byers iron (made by mixing a synthetic slag with a heat of dead-mild steel) is slightly more corrodible. Concerning low-percentage alloy additions, copper is beneficial when the steel is exposed in the open air, but not in enclosed atmospheres (railway tunnels, &c.). Chromium, silicon, nickel and probably arsenic all improve the corrosion resistance.

In general, the surface condition in which the specimens are exposed has little influence on the relative results for different materials, except that in the case of certain wrought irons with mill scales that are particularly resistant to weathering, abnormal results may be obtained for specimens exposed in the as-rolled condition, owing to the accumulation of rust between the scale and the metal which leads to local corrosion. Machined surfaces corrode more than sand-blasted ones. To ensure complete scale removal, by weathering, from $\frac{3}{8}$ -in. plates of ordinary mild steel, exposure for about one year is necessary in Britain; under the milder conditions overseas descaling may be incomplete after five years' exposure. Copper in the steel does not affect the descaling period. The method of piling employed in making wrought irons has little effect on their resistance to corrosion, except that rerolling the puddled bars causes a marked improvement, which may be attributed to the consolidation of the surface. Further reworking has little effect.

The rate of atmospheric corrosion varies with the height above ground-level, but is also governed by local conditions. Horizontal surfaces corrode more than vertical ones, probably because rain water lingers on them and they remain wet longer.

Hot-galvanised mild-steel specimens exposed in a rural atmosphere in Wales showed little sign of deterioration of the zinc coating after eleven years. The probable lives of galvanised coatings are calculated on the basis of test results obtained on zinc specimens exposed at the corrosion stations. For equivalent corrosion resistance there is a marked difference between the gauges of galvanised and black plates; the latter need to be appreciably thicker.

The Corrosion and Fouling of Ships. G. D. Bengough and V. G. Shephard. (Institution of Naval Architects: Engineering, 1943, vol. 155, Apr. 30, pp. 358-360; May 7, pp. 378-380; May 21, pp. 416-417). Methods proposed for the suppression of corrosion and fouling have usually been based on the use of special alloys, electrical systems, and paints and compositions. The Corrosion Committee of The Iron and Steel Institute have experimented for some years in the hope of finding a low-alloy steel which would have a better

corrosion resistance to sea water and at the same time fulfil ship-building requirements and not be too costly. No steel possessing all the required properties is at present in sight, and the application of paints and compositions seems to be the method most worthy of study. Bottom composition schemes generally consist of one or more anti-corrosion coats, followed by one relatively thick anti-fouling coat. The behaviour of the paint scheme must be considered as a whole. The protective success of a complex paint scheme depends, in the first place, on the adhesion of the first or priming coat to the ship's plate. Plates usually undergo one of three treatments before they are painted in the shipyard, namely, acid pickling followed by weathering, weathering only, and weathering followed by a period of immersion in water during fitting-out, the first coat of anti-corrosion composition not being applied until the final docking. All three are followed by scratch-brushing before painting. The first treatment is the general practice in the Royal Navy, and the second is commonly applied in the Merchant Navy. J. C. Hudson has reported that a thinned red-lead paint which can cover 1500 sq. ft. per gal. has been used as a temporary form of protection on both pickled and unpickled plates (weathered for 21 and 35 days, respectively) and caused a marked improvement in subsequent underwater tests. It is unlikely that temporary protective treatments at the rolling mill, or immediately after pickling, would be satisfactory in the shipbuilding industry. It is in the early lives of ships that methods of preventing corrosion not based on impermeability are most necessary. Zinc and barium chromates may be better than red lead for continuously submerged areas. To meet the difficulty caused by moisture on the plate at the time of application, J. E. O. Mayne is developing water-emulsion paints, the constituents of which take up moisture into the paint before drying, and thus make for themselves a good seat on the steel plate.

Information is given on the animals and plants which constitute the fouling on ships, their distribution, habits of reproduction and growth and their association into communities large enough to interfere with the progress of the ship; this part of the paper is based on the First Report of the Marine Corrosion Sub-Committee (*see Journ. I. and S.I.*, 1943, No. I., pp. 339 P-420 P).

Advantages and Objections to the Salt Spray Test from an Electroplating Point of View. A. Hirsch. (Proceedings of the American Electroplaters' Society, Twenty-Ninth Annual Convention, June, 1941, pp. 11-14). The author briefly reports on results of salt-spray tests on electroplated steel (chromium, zinc, cadmium and nickel coatings), and discusses the advantages and, especially, the disadvantages of salt-spray testing, his principal objections being that this test does not simulate corrosion in sea air, and that it takes too long to get the final results.

Comparison of Salt-Spray and Ocean Spray Testing. C. E. Heussner. (Proceedings of the American Electroplaters' Society,

Thirtieth Annual Convention, June, 1942, pp. 75-88). The author carried out sea-water and salt-spray tests at 72° and 95° F. on panels of steel S.A.E. 1010 plated with nickel and nickel + chromium by various methods. The apparatus used and the experimental procedure are described, and the analysis of the sea-water is given. The salt solution contained as a rule 20% of sodium chloride. The investigation led to the following results: (1) In spray tests, panels plated with nickel and chromium show a greater advantage over plain nickel-plated ones than they do in open-air exposure tests. (2) The thickness of the coatings and the mode of their preparation greatly affect the results. (3) At 95° F. the sea-water spray test is more severe than the salt-spray test, whereas the results are nearly equal at 72° F. This difference in the effect of temperature is thought to be due to differences in the amounts of oxygen dissolved in the two solutions. Because of this greater temperature sensitivity in the sea-water test, the author concludes that salt-spray testing is more suitable for practical purposes.

BOOK NOTICES

(Continued from pp. 61 A-62 A)

AMERICAN SOCIETY FOR METALS. *National Emergency Steels*. 6th Printing, 2nd Complete Revision. 4to, pp. 72. Cleveland, Ohio, 1943: The Society.

Due to the shortage of alloying elements and the continual expansion in the production of alloy steels in the United States, it became imperative to conserve the consumption of alloying elements and to introduce new methods of heat treatment. This has been done at the request of the War Production Board by the introduction of a series of steels exhibiting physical properties adequate to replace the standard steels formerly used. This publication sets forth full particulars of the composition, properties, including hardenability curves obtained from the end-quench test, and recommended heat treatments of these National Emergency Alternate Steels or, as they are more familiarly known, NE Steels. The details given are largely from material first published in *Metal Progress*. The NE Steels do not embrace the following types of steel: Low-alloy, high-tensile steels which are furnished as flat rolled products and which require no heat treatment before use, stainless steels or irons such as the high chromium or chromium-nickel types; medium chromium (2-10% chromium) steels which sometimes contain other elements and which are used to resist scaling at elevated temperatures; or any class of tool steel, either carbon or alloy.

BORTH, C. "*True Steel. The Story of George Matthew Verity and His Associates.*" 8vo, pp. 319. Illustrated. Indianapolis and New York, 1941: The Bobbs-Merrill Co. (Price \$3.00.)

This book tells of the life and work of George Matthew Verity, the son of a Methodist preacher, who started without capital or special qualification and became one of the leading American steel executives. It also tells of the part he played, and of those men, Carnahan, Reinartz and others, who assisted him, in the development of the American Rolling Mill Co., the manufacture of Armco iron and the introduction of the continuous wide-strip mill.

DESCH, C. H. "*Substitute Materials in War and Peace.*" 8vo, pp. 28. London, 1943 : The Royal Institute of International Affairs. (Price 9d.)

The author relates some of the difficulties experienced by the Germans during the war of 1914-18 owing to the shortage of raw materials brought about by the blockade. It is pointed out that since then the situation has been radically altered, and the general problem of substitution has assumed world-wide importance, no longer confined to materials for military use. The major portion of the brochure is devoted to a discussion of conditions in the present war, and deals with synthetic substitutes for petroleum, substitutes for rubber, plastics, other organic materials and metals. Germany is amply supplied with iron ore, and large stocks of Canadian nickel were built up. The use of nickel has been restricted, and this metal is being largely replaced by chromium and molybdenum. With regard to manganese, the chief steel-producing countries—United States, Britain and Germany—are without native deposits of importance, and while the first two can face the situation by economy combined with importation from other sources, it is likely that the German drive towards the Caucasus was dictated as much by the need for manganese as by that for oil.

The adoption of a substitute may involve far-reaching changes in industrial practice, and this is illustrated by the increased importance of the light alloys and carbide tools.

The author also indicates the considerable savings which can be effected by the use of materials in a more economical way, and concludes that the extensive scale on which substitute materials have been used in the course of the war will have afforded ample opportunity for the assessment of their value. Some will be regarded as having served a temporary purpose, but others will be found to fill an essential place in world industry.

THOMPSON, LILIAN GILCHRIST. "*Sidney Gilchrist Thomas. An Invention and its Consequences.*" 8vo, pp. 328. Illustrated. London : Faber and Faber, Ltd.

This volume was first published in 1940 at the price of 12s. 6d., and the publishers are to be congratulated on re-issuing it at the very much reduced price of 6s. 0d., so making it available to those students with limited means. It tells of the work of Thomas in the introduction and development of the basic process of steelmaking and is well written by his sister. A notice of the book is to be found in *Journal of The Iron and Steel Institute*, 1940, No. II., p. 130 A.

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REFRACTORY MATERIALS

(Continued from pp. 100 A-102 A)

Carbon—A Refractory Material. F. J. Vosburgh. (Steel, 1943, vol. 112, Apr. 5, pp. 106-110, 145; Apr. 12, pp. 118-125, 146, 147). The author compares the properties of carbon blocks with those of other refractory materials. The application of carbon blocks and various carbon pastes for furnaces for producing aluminium, ferro-silicon, ferro-manganese and calcium carbide is discussed. Carbon paste has up to 2% shrinkage on baking into a solid block, but pre-formed blocks, after baking to 1000° C., shrink very little. Blast-furnace hearth linings are giving satisfaction in Europe, but have not been used in the United States. A recent successful application of carbon blocks is for lining Cottrell precipitator towers.

Magnesite Refractories. J. H. Chesters. (Iron Age, 1943, vol. 151, June 3, pp. 46-51; June 10, pp. 75-81). After explaining the fundamental reaction in the production of magnesium hydroxide from sea-water, the author discusses the physical properties of magnesia, how these affect its use in refractory materials, and the following binary and ternary systems: MgO-SiO_2 , $\text{CaO-MgO-Al}_2\text{O}_3$, $\text{MgO-FeO-Fe}_2\text{O}_3$, MgO-CaO-SiO_2 , $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ and Mg-FeO-SiO_2 . The dissociation of magnesium carbonate is very rapid at about 1110° F., and the breakdown temperature of the carbonate is considerably higher than that of the hydroxide. Attempts have been made to assess the value of a magnesite clinker from a single test, but experience has shown that at least five factors should be examined, namely, chemical analysis, specific gravity, crystal size, hydration tendency and firing shrinkage. The grading of the aggregate for magnesite bricks has a marked effect on firing shrinkage; a brick having a high unfired porosity, or a small average grain size, has a high firing shrinkage. The cracking of magnesite brick in driers is, generally speaking, due to the use of soft-fired magnesite, or to the presence of an excessive amount of fine material which hydrates rapidly and causes considerable expansion, or to too high a temperature in the drier. The thermal conductivity of magnesite is very high, but, unlike that of most refractories, it falls off with increasing temperature. The electrical conductivity of magnesite brick is low at room temperature, but is quite considerable at, say, 2730° F.

Vitrification, Crystallinity and Fusibility of Refractories and Slags. J. F. Hyslop. (Metal Treatment, 1943, vol. 10, Summer Issue, pp. 83-86). The vitrification process in refractories is very important, for the fusible matrix has a controlling influence upon the mechanical strength, porosity, resistance to deformation at high temperature, resistance to corrosion and resistance to thermal shock. Crystal size has an important bearing upon the rate of solu-

tion of a refractory, for small, fine crystals are readily dissolved by flux or slag. Refractories noted for their resistance to deformation all have high crystallinity. A curious slag-refractory reaction of practical importance is the corrosion and disintegration caused by magnetite on spinel types of refractories such as chrome and chrome-magnesite; controlled tests have shown that there is no expansion-reaction between chrome, or chrome-magnesite, and ferric or ferrous oxide.

Conserving Foundry Refractories. C. E. Bales and F. McCarthy. (Foundry, 1943, vol. 71, May, pp. 95, 180-182). The authors recommend a double lining of $9 \times 6 \times 4$ -in. blocks for the interior of cupolas up to the charging door, and a $\frac{3}{4}$ -in. space between the back of the blocks and the shell, which should be filled up with clay grouting. Either of the following mixtures is suitable for patching worn linings: (a) Two parts of white silica sand and one part of fireclay; (b) six parts of crushed firebrick and four parts of plastic fireclay.

Causes of Failure of Patching and Daubing Mixes for Foundry Refractory Purposes. A. R. Blackburn. (American Foundryman, 1943, vol. 5, Apr., pp. 50-52). The author discusses the changes from quartz to cristobalite and from cristobalite to tridymite which occur when silica minerals are heated, the volume changes which accompany them, and the liquidus curve in the Al_2O_3 - SiO_2 equilibrium diagram. The effects of lime, magnesia and ferrous oxide on the fusion point of patching refractories used in the foundry are explained.

Sleevebrick and Nozzle Problems. F. F. Franklin. (Steel, 1943, vol. 112, Apr. 26, pp. 94-98). The author describes the manufacture of nozzles for ladles and sleeves for stopper rods. The refractory mixes are de-aired, and are then extruded, or shaped in a spinner press. Sleeves are dried in air at about 130°F . and nozzles at from 180° to 230°F . The apparent porosity of sleeve bricks should be 17-20%. The porosity of stoppers ranges from 8% to 20%, and for teemingforging grades of steel it should be between 12% and 14%.

High Temperature Heat Insulation. G. W. Patterson. (Canadian Ceramic Society: Iron and Steel, 1943, vol. 16, June, pp. 438-442; July, pp. 475-477). See p. 2 A.

FUEL

(Continued from pp. 102 A-104 A)

Practical Turbine Lubrication. S. R. O'Dette. (Iron and Steel Engineer, 1943, vol. 20, Apr., pp. 34-43). The author surveys recent improvements in lubrication systems for steam turbines. The shallow, broad, oil reservoir is giving way to the tall, narrow

one. The area of exposed metal, subject to rusting, is reduced in the new type. The best reservoir design is the tall type combined with a sloping bottom connected to the purifying system at the lowest point. When a high-pressure turbine is being shut down, it may require to be in turning gear for at least 24 hr. to reduce the rotor and casing temperature to about 250° F., at which it can be stopped without fear of distortion; there is often difficulty in maintaining the oil-films at low journal speeds with low-viscosity oil, so that, when a turbine is to be taken off the line, the oil-coolers should be opened wide, in order to reduce the temperature and increase the viscosity of the oil as rapidly as possible. Turbine oils containing wetting agents are now obtainable; these prevent the corrosion of the interior surface of oil reservoirs above the oil level.

Control of Powdered-Coal-Fired Melting Furnaces. J. A. Durr. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-25). The author discusses the fundamentals of the combustion of pulverised coal and stresses the need for standardising melting practice in open-hearth furnaces.

An Experimental Investigation of the British Standard Method for the Crucible Swelling Test for Coal. H. N. Ostborg, H. R. Limbacher and R. A. Sherman. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 851-864). The authors investigated the applicability of the British Standard crucible swelling test for testing American coals. The particle size and small variations in the weight of the sample have little effect on the results. The principal variable that affects the swelling of the coal is the method of heating the crucible. The swelling index was found to be a good indicator for the performance of a coal in small underfeed stokers.

The Removal of Organic Sulphur Compounds from Gases. N. Booth and L. J. Jolley. (Journal of the Society of Chemical Industry, 1943, vol. 62, June, pp. 87-88). Gases such as water-gas, coal-gas and coke-oven gas contain appreciable amounts of organic sulphur compounds, mostly in the form of carbon disulphide and carbon oxysulphide. Experiments conducted at the Fuel Research Station show that these compounds can be removed by washing with water under pressure. The time of contact and amount of water used can be adjusted to give a gas of any desired degree of purity down to the limit of 2.7 grains per 100 cu. ft.

PRODUCTION OF IRON

(Continued from pp. 104 A-105 A)

Brazilian Pipemaker Operates Four Charcoal Stacks. G. A. Maigne. (Steel, 1943, vol. 112, Jan. 25, pp. 69-70, 83). The author describes the activities of Companhia Ferro Brasileiro, manufacturers

of pig iron, centrifugally-cast pipes and fittings. The company operates four charcoal furnaces producing a total of 128 tons of iron per day. Part of the blast-furnace gas is burnt in a Liesen heater to heat the blast to 1100–1300° F. Another portion of the gas is burnt under boilers at a power-station to supply current to the works. In the foundry, two cupolas serve five centrifugal casting machines with water-cooled steel bodies. After casting, the pipes are annealed for 1 hr. at 1475° F. Two of the machines can produce pipes 19 ft. 9 in. long from 3 to 24 in. in dia., two machines are for 9 ft. 10½-in. pipes 2 to 4 in. in dia. and the fifth is a smaller one.

Blast-Furnace Charging Equipment. L. R. Milburn. (*Iron and Steel Engineer*, 1943, vol. 20, May, pp. 47–52). The author describes the following equipment at one of the blast-furnaces of the Great Lakes Steel Corporation: (1) The large and small bells and bell-hoist mechanism; (2) the charge distributor; (3) the stock-height test-rods; (4) the skip-hoist; and (5) the skip-loading equipment.

Some Metallurgical Aspects of Blast Furnace Operation. C. D. Smith. (*Eastern States Blast Furnace and Coke Association: Iron and Steel Engineer*, 1943, vol. 20, May, pp. 33–39; *Blast Furnace and Steel Plant*, 1943, vol. 31, May, pp. 529–537). This paper has been published previously with the title “Blast Furnace Metallurgy” (see p. 72 A).

The Commercialization of Blast-Furnace Slag. F. Hubbard. (*Iron and Steel Engineer*, 1943, vol. 20, June, pp. 33–40). After a historical account of the development of the use of blast-furnace slag, the author discusses the quantities and districts in which it is available in the United States and its uses. About 30,000,000 tons were produced in 1942. The characteristics of air-cooled slag, water-cooled granulated slag and light-weight slag are explained, much of the information being based on a paper by T. W. Parker and J. F. Ryder (see *Journ. I. and S.I.*, 1942, No. II., p. 21 F).

Ore Reduction . . . Use of Gas in Republic Steel's New Sponge Iron Plant. J. J. Craig. (*American Gas Association Monthly*, 1943, vol. 25, Apr., pp. 147–148). A brief account is given of a sponge-iron plant now being built at the works of the Republic Steel Corporation on the authority of the War Production Board. The ore contains about 94.5% of magnetite, and the fuel will be coke-oven gas containing about 56% of hydrogen. A Herreshoff multiple hearth furnace with twelve hearths 20 ft. in dia. will be used. The ore will be charged at the top and will move down from hearth to hearth; its movement on each hearth will be accomplished by blades attached to rabble arms revolving horizontally. Two desulphurising units for the coke-oven gas, a heat exchanger, a preheater, a gas-washer and a Cottrell precipitator will be provided. The hot sponge iron will be discharged from the bottom hearth directly into a briquetting machine. The product is expected to contain about 88.5% of iron and a small amount of unreduced iron oxide.

FOUNDRIY PRACTICE

(Continued from pp. 106 A-112 A)

Some Principles of Melting Malleable Iron. H. A. Schwartz. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-3). The author discusses the theory of the generation of heat when coal and gases are burnt in a furnace and the factors governing the transfer of heat to the charge in the making of malleable cast iron.

Brackelsberg Furnace Melting of Malleable Iron. W. Zeunik and K. Mason. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-4). The authors describe the practice for making malleable iron with Brackelsberg furnaces at the works of the National Malleable and Steel Castings Co., Indianapolis. There are three 8-ton furnaces, each measuring 14 ft. long \times 48 in. in inside dia. The shell has two steel tyres, on which it can be rotated at 1.37 r.p.m. The shell can be tipped on the transverse axis passing through the centre of gravity. The furnace stack has a double lining for about half its height, and the annular space between the two linings, which are made of specially shaped fireclay blocks, is used to preheat the secondary air. The fuel is a pulverised soft West Virginia coal. The furnace is lined with silica bricks, and with proper care the linings last from 100 to 200 heats. The furnace is tipped to about 45° for charging, and a typical charge consists of scrap 8750 lb., pig 1250 lb., ferro-silicon 25 lb., ferro-manganese 12 lb. and petroleum coke 50 lb. The coal is fed at a rate of about 15 lb. per min., and the shell is kept stationary for the first 20 min.; it is then rotated one-quarter of a turn at 10-min. intervals to bring the underneath portions of the charge to the surface. A 5-ton heat of low-carbon malleable iron can be made in 2 hr. from turning on the fuel to tapping, with a coal consumption of 350-450 lb. per ton of metal melted.

Open-Hearth Furnace for Production of Malleable Castings. L. J. Kelly. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-5). The author briefly describes the open-hearth practice at the Fort Pitt Malleable Iron Co., Pittsburgh, where there are three oil-fired open-hearth furnaces of 45, 25 and 20 tons capacity respectively. The charge is made up of pig 38%, sprues 45%, malleable scrap 15% and steel scrap 2%. The total time for charging, melting and refining is 7-10 hr. Two or three slag-skimming operations with a water-cooled skimmer are required. Temperatures of 1650° C. in the furnace and 1575° C. at the spout are regularly attained. The furnaces are also equipped to burn natural gas, and at week-ends and other shut-down periods it has been found very economical to use natural gas and low-pressure air to keep the furnace hot.

The Cupola/Air-Furnace Duplex Process for Production of Malleable Cast Iron. F. J. Wurscher. (American Foundrymen's

Association, Apr., 1943, Preprint No. 43-28). The author describes the plant and practice for making malleable cast iron at the foundry of the Acme Steel and Malleable Iron Co., Buffalo.

Steel-Foundry Practice. D. O. Davis. (American Society for Metals: Canadian Metals and Metallurgical Industries, 1943, vol. 6, May, pp. 23-26). The author describes the steel-foundry practice at the works of Dominion Foundries and Steel, Ltd., Hamilton, Ontario, where there are facilities for making castings of up to 120 tons.

The Effect of Resin Binder Additions on the Properties of Moulding Sands. E. Pragoff, jun., and C. P. Albus. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 337-375). The authors report on an investigation of the effect of additions of a pulverised high-softening-point resin on the physical properties of two synthetic moulding sands. The general conclusions were that the addition of resin has the following effects: (1) The green strength is increased; (2) the permeability decreases slightly; (3) the dry strength is greatly increased; (4) the hardness of the mould is increased; (5) it retards the loss of strength of dry-sand moulds exposed to a moist atmosphere; (6) it has little effect on expansion, but considerably reduces the contraction; (7) it causes a considerable quantity of gas to be generated during pouring; this gas is reducing in character; and (8) it reduces the tendency of some sands to crack during rapid heating to 2500° F.

Progress Report—Comparison Data on the Durability of Naturally-Bonded and Synthetic Molding Sands by the Repeated Pour Test. J. CoVan. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 539-561). The author reports the results of durability tests on naturally-bonded and synthetic moulding sands undertaken for the Subcommittee on Durability of the Sand Research Committee of the American Foundrymen's Association. A Midwestern State and an Eastern State natural sand and three synthetic sands, bonded with montmorillonite, illite and kaolinite respectively, were used. The amount of natural clay bond needed to produce the required 6 lb. per sq. in. green compression strength throughout each series of ten casts was at least twice as much as that required for synthetic sands.

A Study of the Flowability of Foundry Sands. E. O. Lissell and E. J. Ash. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 637-653). The authors report the results of flowability tests on Ottawa round grain and angular grain silica sand carried out by measuring the pressure applied to the sand in an American Foundrymen's Association standard specimen container and extruding the sand through the 1-in. hole in the cover. The effect of adding linseed oil was to lubricate the grains and obtain close packing without external pressure. Water, on the other hand, increased the intergranular friction and tended to separate the grains, making a certain degree of compression possible.

Southern Bentonite in the Steel Foundry. N. J. Dunbeck. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-7). The author compares the properties of the southern and western bentonites which are found in the Mississippi district and in Wyoming respectively. The former swells in water to about ten times its dry volume, whereas the latter swells very little.

Gating Malleable and Arma Steel Castings. F. E. Reeves. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 568-592). The author describes many examples of the gating and riser practice adopted at the Saginaw Malleable Iron Division of the General Motors Corporation for reducing the amount of scrap and rejects in the production of malleable iron castings.

A Novel Idea for Correctly Coring Machine-Made Moulds. G. R. Wilkinson. (Foundry Trade Journal, 1943, vol. 70, June 3, pp. 96, 88). The author describes a method of setting a core in a machine-made mould for an elbow 12 in. long with a $3\frac{1}{2}$ -in. bore. A cast core-iron, carrying projecting nails bent to the contour of the core-box, is rammed in the top half of the core. The core-prints are extended so as to make the core self-supporting, thereby eliminating the use of chaplets.

Recent Developments in Core Moulding and Drying. A. G. Arend. (British Steelmaker, 1943, vol. 9, May, pp. 350-353). The author describes a modern machine and drying equipment for the high-speed production of sand-cores.

Infra-Red Lamps Dry Green Sand Molds for War Castings. L. M. Duryee. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-6). The author gives some details of the infra-red lamp equipment for drying green sand moulds. The lamps are mounted on frames carrying 30-50 lamps. Each bulb is rated at 250 watt and 110 V. The labour of three men, formerly using torches and charcoal, has been eliminated by the new method. The average time for drying a mould is 90 min.

Centrifuging after the Mold is Filled with Steel. W. F. Wright and J. B. Caine. (Foundry, 1943, vol. 71, May, pp. 91-93, 175, 176).

Centrifuging after Filling the Mould. W. F. Wright and J. B. Caine. (Iron Age, 1943, vol. 151, May 20, pp. 64-68). The authors describe examples of the centrifugal casting of steel in which the mould is rotated on a vertical axis after the steel has been poured. The centrifugal force acting on a 24-in. dia. gear rotating at 92 r.p.m. will increase from zero at the centre to 2.5 lb. per sq. in. at the periphery. The total force tending to move the steel to the rim in this case amounts to the atmospheric pressure plus 2.5 lb. per sq. in. plus 1.5 lb. per sq. in. due to a 6-in. head of metal. Steel can, however, develop a strength of over 100 lb. per sq. in. before it has completely solidified, so that spinning the mould, if commenced when the steel has begun to solidify, would not exert sufficient pressure on the metal to fill shrinkage cavities. When changing

from the ordinary method to the centrifugal method of casting wheels it is necessary to increase the spoke and web thickness of the ordinary design.

Centrifuging during Pouring. A. Johnson. (Iron Age, 1943, vol. 151, May 20, pp. 62-64). The author describes the centrifugal casting of steel sheaves in vertical spindle machines. In this case the mould is spinning while the metal is being poured.

Track Shoe Production. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, May, pp. 16-17, 20). A brief description is given of the operations at Hull Steel Foundries, Ltd., in Canada, where large numbers of tank-track shoes of high-manganese steel are cast.

Casting Cleaning in a Gray Iron Foundry. H. B. Nye. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 499-510). The author reviews the advantages and disadvantages of the following equipment for cleaning castings: (1) Tumbling barrels; (2) air-blast barrels; (3) barrels in which the abrasive is propelled by centrifugal force without compressed air; (4) air-blast rooms; and (5) air-blast tables. In comparing the costs of some of these processes, method (2) was found to be much dearer than method (3). The centrifugal blasting cabinet was also much cheaper to use than tumbling for cleaning cast air receivers 19 in. high \times 19 in. in dia.

Grinding Wheel Cost Control. J. A. Westover. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 595-606). The author describes the measures by which the grinding costs at a Chicago steel foundry were reduced by 30%. Performance records for each type of wheel were obtained; these showed the ratio of the loss in weight of the wheel in ounces to the weight of metal removed in pounds for different wheel pressures. When labour rates are low a wheel with a long life and a comparatively slow rate of metal removal was chosen, and *vice versa*. A method of establishing a scale of wages which, as well as providing a production incentive, also encourages the maintenance of a low ratio of wheel wear to metal removal, is explained.

Ingot Mould Defects Caused by Blacking. W. S. Williams. (Iron and Steel, 1943, vol. 16, July, pp. 471-482). The Quasi-Bessemerising process of making ingot moulds of hematite iron has already been described (*see* Journ. I. and S.I., 1943, No. I., p. 80 A). In the present paper the author discusses defects which arose on some of the moulds; these consisted of surface markings, raised flat areas on the outside and a perforated interior surface. They were found to be caused by putting too thick a coating of blacking on the moulding sand. On analysis, such carbon was confused with the free carbon always present in hematite iron. This additional carbon was diffused through the ingot-mould wall, and deprived the iron of its erosion-resisting properties, so that even side splashes of molten steel striking the side of the mould could cut deeply into it.

Ordinance Inspection of Castings. A. C. Richmond. (Iron Age, 1943, vol. 151, Apr. 22, pp. 41-44). The author discusses types of defects found in castings for ordnance work, their probable cause and the methods by which they are detected.

A Study of "Burnt-On" or Adhering Sand. J. B. Caine. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-24). In a study of the mechanism causing sand to be burnt on to steel castings the author found this to be due to the steel penetrating into the sand and mechanically locking it on to the casting. Adherence caused by fusion plays only a minor part. Decreasing the void size by decreasing the grain size of the sand reduces the penetration of the metal and the amount of sand adhering to the casting, but the refractoriness of the sand is also lowered. The action of silica flour, whether added to the sand-mix or as a mould-wash, is complex. A mixture of the fine flour and the coarser grains of the base sand increases metal penetration and sand adherence, but a uniform face of fine silica flour in contact with the molten metal decreases penetration and sand adherence up to a point which depends on the temperature of the sand-metal interface. Beyond this point the silica flour breaks down suddenly and bad burning-on occurs.

Statistical Methods as an Aid to the Control of Foundry Operations. H. H. Fairfield. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 611-634). The author shows, with examples, how frequency curves and other statistical methods can be employed in a grey iron foundry to trace the causes of changes in the quality of castings.

PRODUCTION OF STEEL

(Continued from pp. 112 A-115 A)

Relation of Flame Character to Open Hearth Operation. A. J. Fisher. (Iron and Steel Engineer, 1943, vol. 20, May, pp. 61-74). The author describes the system developed by the Bethlehem Steel Corporation for observing and recording the radiation of the flame in oil-fired open-hearth furnaces and relating it to the tonnage of steel produced per hour. The radiation recording equipment consists of an indicating and recording potentiometer mounted on a rubber-tired wheelbarrow which is moved to the instrument panel for each furnace and plugged in, and a long-handled radiation tube. The tube has a special frame for centering it in the wicket hole in the furnace door; it has a mica screen and is sensitive to wave-lengths in the 0.2-5.0 micron range. Readings are taken after the lime boil when the furnace is quiet. The observer places the tube in position at the lower edge of the flame, and then, while observing the indicator dial, depresses the handle, thus causing the tube to move

through the flame from bottom to top. Readings are taken with the tube manipulated through the first and second doors from the burner end. In order to obtain comparable readings the following conditions are kept constant at the time of observation : oil flow, oil temperature, air flow, pressure of steam for atomising and furnace pressure. By relating flame radiation readings to furnace output over a considerable period, valuable data have been collected which enabled the furnace superintendents to issue advance furnace operation schedules which maintain maximum production throughout a campaign.

Principles of the Open-Hearth Melting Furnace in the Steel Industry. F. A. Melmoth. (American Foundrymen, 1943, vol. 5, May, pp. 4-7). The author gives a concise description of the open-hearth process of making steel.

The Manufacture of NE 1330 Steel by an Open Hearth Melter. E. G. Wigfield. (American Institute of Mining and Metallurgical Engineers : Blast Furnace and Steel Plant, 1943, vol. 31, May, pp. 513-515, 520, 521). The author describes the trials, errors and the final procedure adopted for making steel NE 1330 at a basic open-hearth plant using ferro-manganese additions in the furnace and ferro-silicon additions in the ladle. The composition of steel NE 1330 is : carbon 0.28-0.33%, manganese 1.60-1.90%, silicon 0.20-0.35%, sulphur 0.045% max. and phosphorus 0.040% max.

Presses for Briquetting and Baling Steel Scrap. W. L. DeLaney. (Steel, 1943, vol. 112, May 3, pp. 102-104, 141, 142). The author describes several types of baling presses for briquetting turnings and other forms of light scrap. One 325-ton machine making 8 strokes per min. produces 3 tons of briquettes, 6 in. in dia. and $3\frac{1}{2}$ in. high, per hr.

The Economic Utilisation of Alloy Steel Scrap. H. Bull. (Sheffield Society of Engineers and Metallurgists : Iron and Steel, 1943, vol. 16, June, pp. 432-437). The author discusses how turnings and other forms of alloy-steel scrap can be used by the steel-maker. The density of the scrap is often expressed as a grade number which is the weight in hundredweights of 1 cu. yd. Turnings can be broken down into chips in machines. Nickel-chromium steel turnings of 2-6 grade are converted to grade 30 by chipping, whereas nickel case-hardening steel turnings after chipping do not grade higher than 18. Pre-melting is favoured to-day as a means of utilising mixed alloy-steel turnings. In the "S.P.B." (Sheffield Process Basic) practice of making alloy steel, the charge put in the furnace contains all the alloying elements required to give the analysis specified, plus the usual margin of carbon; the bath should contain about 0.5% of silicon and a maximum amount of manganese. Melting and slag difficulties are not experienced if the chromium-bearing materials are charged first and covered with carbon steel turnings, the limestone and hematite iron being added last. The melted charge has a thin slag. The bath is allowed to get hot before

ore is fed in small amounts. The carbon falls quickly; when the iron content of the slag falls the boil is finally checked with ferro-silicon.

Welded Ladles Help Increase Steel Output. G. R. Reiss. (Steel, 1943, vol. 112, May 17, pp. 112-115). The author discusses the advantages of using welded instead of riveted ladles. There is a considerable saving in the weight of welded ladles when their capacity exceeds 50-60 tons.

Transmission-Line and System Problems in Supplying Large Electric-Arc Furnaces during Wartime. B. M. Jones. (Electrical Engineering, 1943, vol. 62, Apr., pp. 197-202). The author discusses some of the data and calculations necessary to solve the problem of the method of connecting electric-arc furnace loads to a transmission system, and gives information on the methods adopted for medium and large furnaces at ten American steelworks.

Inserts Increase Life of Ingot Mold Stools. F. G. Norris. (Iron Age, 1943, vol. 149, Mar. 5, pp. 63-64). A brief illustrated description of an improved design of ingot mould stool is given. It consists of a cast-steel frame within which is cast an iron plate. When the ingot is poured the molten steel is in contact with the iron plate only, and when cracking eventually takes place it is only the plate which requires renewal.

The Structure and Segregation of Two Ingots of Ingot Iron, One Containing Lead. L. Northcott and D. McLean. (Iron and Steel Institute, 1943, this Journal, Section I). The object of this investigation was to determine the segregation in a low-carbon steel ingot containing lead as compared with a similar ingot free from lead. For this purpose two ingots were obtained from the same melt, a lead addition being made to the mould in one case but not the other. The axial faces of the ingots were prepared for macro-examination, sulphur- and lead-printing, and samples were obtained for chemical analysis, micro-examination and radiographic examination. It was found that, apart from noticeable lead segregation at the extreme base of the ingot, the distribution of lead was very similar to that of the other elements examined. Machinability tests on sections cut from the cast ingot confirmed that the energy absorbed in machining the lead-bearing steel was 25% less than with the lead-free steel.

FORGING, STAMPING AND DRAWING

(Continued from pp. 115 A-116 A)

All-Hydraulic Press is Now Adapted Successfully to Forging Operations. A. F. Macconochie. (Steel, 1943, vol. 112, May 17, pp. 100-101, 149, 150). The author points out the advantages of

the all-hydraulic press for forging hot billets and other heavy work as compared with the steam-hydraulic press. He describes the "Fastraverse HPM" all-hydraulic press.

Shell Forging on Bulldozers. W. Trinks. (American Society of Mechanical Engineers: Heat Treating and Forging, 1943, vol. 29, May, pp. 227-230, 244). The author describes briefly three ways in which "bulldozer" forging machines can be adapted to forging shells. The bulldozer is a forging machine, usually horizontal, in which a wide crosshead, or traverse, is slowly reciprocated by two connecting links, one on each side of the machine. In the progressive pierce-and-draw method the shell forging is pierced in three stages, and it is moved manually from one die to the next. When the machine is used for piercing only, the piercing stroke is short and the forgings are elongated by a subsequent process. In what is called the French extrusion process, the blank is placed in a container from the rear end of which extends a punch or mandrel; this mandrel remains stationary and the blank, guided in a stationary tubular die, is extruded over the mandrel by a ram moving in the die.

Forging Operations Feature Production of Steel Cartridge Cases at Buick. R. B. Schenck. (Society of Automotive Engineers: Heat Treating and Forging, 1943, vol. 29, May, pp. 236-241). The production of steel cartridge-cases at the Buick plant of the General Motors Corporation is described (*see* pp. 46 A and 115 A).

Steel Cartridge Cases and How Buick Makes Them. (Steel, 1943, vol. 112, May 3, pp. 92-95, 135-139). A description is given of the sequence of processes in the manufacture of steel cartridge-cases for 75-mm. shells at the Buick Motor Division of General Motors Corporation.

Co-operative Research in the Wire Industry. A. T. Adam. (Metal Treatment, 1943, vol. 10, Summer Issue, pp. 105-110, 126). The author reviews the fundamentals of wire-drawing and points out that these are applied in different ways in different wire-drawing shops. He accordingly stresses the need for more co-operative research in the wire industry so that the techniques for producing the optimum properties in different types of wire may be more clearly defined and recognised.

PYROMETRY

Temperature Measurement and Control with Solid Photoelectric Cells. M. E. Fogle. (Electrochemical Society, 1943, Preprint No. 83-14). The author discusses the advantages of using "solid" photo-electric cells as a means of measuring and controlling the high temperatures encountered in metallurgical industries. These cells are also known as the "blocking layer" type, and usually comprise a layer of selenium coated on a metal disc with a thin transparent

layer of gold or platinum on top. The radiant energy passing through this transparent layer is absorbed near the upper surface of the selenium layer, and sets free electrons which tend to flow to the transparent metal film. Data on the spectral sensitivity of these cells are presented and the advantages of using them in preference to photo-tube pyrometers are pointed out.

The Measurement and Control of Liquid Steel Temperatures. T. Land. (Journal of the Society of Glass Technology, 1943, vol. 27, Feb., pp. 22-31). The author gives an account of the application of quick-immersion thermocouples to the measurement of liquid steel temperatures in open-hearth, electric-arc and high-frequency induction furnaces and in Bessemer converters. Details are given of the equipment and procedure essential to ensure satisfactory results, and data are quoted to illustrate the value of the measurements which can be made.

Temperature Measurement of Molten Cast Iron with the "Rayotube" and Optical Pyrometer. R. H. Koch and A. E. Schuh. (Transactions of the American Foundrymen's Association, 1943, vol. 50, June, pp. 1163-1179). The authors describe the "Rayotube" temperature-measuring instrument, how it was set up to determine the changes in temperature of the metal leaving a cupola spout and the advantages and limitations of an optical pyrometer for the same purpose. The Rayotube consists of a tube of refractory material with a thermopile and a quartz lens at the upper end, and a water-jacket for cooling round the upper half of the tube. The lower end is sealed, and this, when immersed in the metal, is raised to the temperature of the latter; the radiation from it is directed by the lens on to the thermopile, which is connected to a suitable recording potentiometer. A current of air is also passed through the inside of the tube to remove any fumes. A proprietary clay-graphite has proved to be the most satisfactory material for the refractory tube, with an average life of three 16-hr. heats with continuous immersion. The usefulness of this instrument in assisting cupola control has been proved in practice.

HEAT TREATMENT

(Continued from pp. 117 A-119 A)

Flame Hardening from the Metallurgical Viewpoint. M. L. Becker. (Metal Treatment, 1943, vol. 10, Summer Issue, pp. 71-81, 132). The author discusses the metallurgical aspects of flame hardening and the need for adequate control tests. Any steel or cast iron containing more than about 0.35% of carbon is potentially suitable for flame hardening; for carbon steels the usual range is 0.40-0.70%. The use of alloy steels in place of plain carbon steels, has little justification insofar as the properties of a normally pro-

duced flame-hardened case are concerned. The gradual merging of the hardness curve into the core-hardness line is usually absent in flame hardening and, if the steel has been previously hardened and tempered, the hardness immediately beneath the case tends to be less than that of the core. Flame-hardened parts cannot be relied on to give a resistance to fatigue comparable with case-hardened or nitrided parts of similar case hardness and core strength, so that a flame-hardened gear or pinion must be considerably larger and heavier than a case-hardened one for the same duty.

What the War Period Is Doing to Metal Treating with Gas. J. P. Brosius. (American Gas Association Monthly, 1943, vol. 25, Apr., pp. 162-164). The author points out how war conditions have stimulated the use of gas for such processes as flame hardening and the heat treatment of metals.

The Heat Treatment of Steel with Particular Reference to Small Forgings. E. Gregory. (Engineering Inspection, 1943, vol. 8, Summer Issue, pp. 4-11). After a brief consideration of the iron-carbon diagram the author shows how this is applied to determining the correct heat-treatment temperature for forgings. The difference between overheated and burnt steel is stressed. The coarse structure associated with overheating can be readily refined, whilst burning is associated with surface decarburisation and the penetration of oxides; oxide films cannot be removed by heat treatment. Forging defects include the pressing of oxide particles into the steel being worked. In consequence of their air-hardening properties, "martensitic" steel forgings and drop forgings should always be carefully cooled after forging to shape, and they must be protected from draughts of cold air. Some drop-forgers transfer the hot forgings immediately into a hot softening furnace. The tendency to crack in the hardening process can be reduced by reversing the temperature gradient at the surface of the steel before quenching. This can be achieved either by allowing some time to elapse between withdrawal from the furnace and plunging in the cooling agent, or by deliberately lowering the temperature of the furnace 5-10° C. before withdrawal for quenching.

Controlled Atmospheres for Heat-Treatment Processes. S. V. Williams. (Metal Treatment, 1943, vol. 10, Summer Issue, pp. 111-121). The author discusses developments of the use of derivatives of ammonia, hydrocarbons and carbon as artificial atmospheres for the heat treatment of ferrous and non-ferrous metals. The I.C.I. ammonia cracker and the G.E.C. charcoal burner are described.

Controlled Atmosphere Indicator. C. A. Hansen, jun. (General Electric Review, 1943, vol. 46, Apr., pp. 221-222). The author describes an instrument for continuously testing the composition of heat-treatment furnace atmospheres. It is based on detecting, by electrical means, changes in the thermal conductivity of the gas mixture.

Proposed Method for Test for Effect of Controlled Atmospheres upon Alloys in Electric Furnaces. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 180-183). This paper constitutes an appendix to the Report of the A.S.T.M. Committee B-4 on Electrical Heating, Electrical Resistance and Electric-Furnace Alloys. A detailed description is given of a proposed method for testing the action of commercial protective atmospheres upon the heat-resisting alloys used for the elements in electric heat-treating furnaces, as well as a method of determining the temperature at which attack occurs and the effect of stress upon the rate of attack.

Measuring Furnace Atmospheres. F. B. Leslie. (Iron Age, 1942, vol. 149, Mar. 5, pp. 60-62). The author describes the principle of the Ranarex analyser which is used to indicate changes in the composition of heat-treatment furnace atmospheres. The instrument consists of two impellers, each exerting a torque upon separate impulse wheels; one impeller is driven by a current of air and the other by the furnace gas, both being brought to the same temperature and degree of humidity. Any change in the density of the furnace gas affects the torque on the impulse wheel and, as the two impulse wheels are connected to a pointer by a sensitive linkage arrangement, changes in the gas composition which affect the density are shown.

Gas Fired Industrial Furnaces of the War and Post War Period. E. G. De Coriolis. (Heat Treating and Forging, 1943, vol. 29, May, pp. 233-234, 247-249). The author discusses some war-time developments in gas-fired industrial furnaces. Mention is made of radiant-tube roller-hearth furnaces with extensions which form cooling zones. In the heat treatment of special steel tubes for aircraft construction the tubes are cooled by a prepared refrigerated atmosphere, which is directed on them by fans placed above and below the conveyor; about half of the heat absorbed as the tubes pass through the 55-ft.-long heating zone is given up to the atmosphere in the first 4 ft. of the cooling zone.

Automatic Furnace Hardens 200 Three-Inch Shells per Hour. (Industrial Heating, 1943, vol. 10, Apr., pp. 490-492). A brief description is given of a continuous gas-fired furnace for hardening 3-in. shells. Four parallel channels pass right through the furnace to the chute to the quenching tank, and separate hydraulic pushers move the shells along these channels. The pushers are electrically controlled and timed to operate in sequence so that only one shell is discharged at a time.

Induction Hardening. (Commonwealth Engineer, 1943, vol. 30, Mar. 1, pp. 183-186). The theory and practice of induction hardening are explained. In view of the extremely rapid transformation of pearlite to austenite accomplished by induction heating and the tendency for this to occur between the lower and upper critical points, a considerable amount of free ferrite might be expected. Free ferrite does not form, however, unless the heating is stopped at the

instant diffusion has been completed within the ferrite boundaries. There is a preferential removal of carbides over ferrite, and a major portion of the ferrite persists until most of the carbides have become diffused. Induction heating apparently has a stimulating effect on carbide solution and the production of a homogeneous austenitic condition. Not only is the time requirement reduced, but a further refinement occurs producing a higher hardness than on an identical piece furnace heated and quenched to the maximum hardness possible by the older method. The acicular martensitic structure resulting from conventional methods is absent; instead, a more homogeneous and nodular martensite of greater fineness is found; this difference is more readily apparent with carbon steels than with alloy steels. New applications for induction heating include hardening a piece of steel and simultaneously brazing it to copper, and the tempering of a small section of a previously hardened part to render that section machinable.

Quench-Time Control for Cast Armor. J. P. Vollrath. (Iron Age, 1943, vol. 151, Apr. 22, p. 59). The author briefly describes an automatic quenching control mechanism for the quenching of cast-steel armour plate. The plate comes out of the heat-treatment furnace suspended from an overhead conveyor rail, a section of which can be lowered and raised by a compressed-air cylinder. The operation of the cylinder is controlled by a solenoid valve in the air line, and this valve is in turn controlled by a timing switch which can be set to any desired quenching time. The quenching tank is situated immediately below the movable section of the conveyor rail.

Straightening Heat-Treated Parts. G. B. Berlien. (Steel, 1943, vol. 112, Mar. 15, pp. 114, 137, 138; Mar. 29, pp. 74, 98; Apr. 12, pp. 112, 140). In the first section of this paper the author describes steps which can be taken to reduce the distortion of oil-quenched parts; these include: (a) For parts which vary in thickness, the heavy section should enter the oil-bath first; (b) reamers, broaches and other parts with flutes should be placed in a chuck on a vertical spindle and lowered into the oil while spinning; and (c) steels which harden right through can usually be removed from the bath while still at 400–500° F. and straightened in a press while still hot. In the second and third sections methods of straightening parts which have been distorted are described. One method is to apply local heating with an oxy-acetylene torch on the convex surface of a distorted part.

Draw Straightening of Heat-Treated Parts. G. B. Berlien. (Steel, 1943, vol. 112, May 3, pp. 98, 140). The author describes examples of the application of a process of straightening by tempering to parts which have been distorted in heat treatment. The parts are first tempered at a low temperature and then put in some form of clamp to straighten them, and finally tempered at a higher temperature. Ring gears of 0.45% carbon steel, for example, were tempered first at 375° F. and then at 500° F.

Heat Treatment of Medium Carbon Cast Steel in Moderately Heavy Sections. K. L. Clark, H. F. Bishop and H. F. Taylor. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-27). The authors describe an investigation at the American Naval Research Laboratory of the effects of different heat treatments on two cast low-alloy steels containing carbon 0.24% and 0.27%, copper 0.21% and 0.17%, nickel 0.75% and 0.73%, and chromium 0.22% and 0.19% respectively. Rectangular test-blocks measuring $10 \times 10 \times 20$ in. and two smaller sizes were used. It was found that the long annealing cycle for moderately heavy castings could be replaced by a form of heat treatment taking approximately one-third of the time originally specified without detriment to the physical properties. In fact, the yield ratio, reduction of area and notched-bar impact strength could be raised materially without adversely affecting the tensile strength.

WELDING AND CUTTING

(Continued from pp. 120 A-121 A)

How to Recondition Worn Pump Shafts and Rods. (Mechanical Topics: Welding Journal, 1943, vol. 22, Apr., pp. 248-249). Illustrated descriptions are given of the welding and metal-spraying methods of building up worn pump-rods and shafts.

High-Speed Steel-Tipped Tools Made Quickly and Cheaply by Welding Salvaged Parts. C. B. Ericson. (Steel, 1942, vol. 112, Feb. 1, pp. 94-96). The author describes a simple technique for welding high-speed steel tips to carbon steel shanks (*see* Journ. I. and S.I., 1943, No. I., p. 208 A).

Silicon Loss between the Rod and the Deposited Metal in Oxy-Acetylene Welding of Cast Iron. R. M. Allen, F. F. Dennis and G. Swartz. (Welding Journal, 1943, vol. 22, Apr., pp. 179-S-181-S). The authors report on an investigation of the silicon loss which occurs between welding rod and deposited metal in the oxy-acetylene welding of cast iron. Rods with silicon contents in the 2-6% range were used. No clear correlation between the silicon contents of rod and weld could be established, although the percentage loss tended to be higher with increasing silicon in the rod. When the silicon content of the rod was less than 2.50% the physical properties of the weld were seriously affected. The best welds were obtained with 2.75-3.50% of silicon. The silicon loss was not affected by the nature of the flame.

Welding Electrodes. J. W. Miller. (Wire and Wire Products, 1943, vol. 18, May, pp. 279-281, 307, 312). The author discusses the composition of coatings for welding electrodes.

Spot Welded Aluminium-Clad Steel. J. D. Rosenblatt. (Iron Age, 1943, vol. 151, June 10, pp. 72-74). The author reports

briefly on the results of tests from which the best technique was established for spot-welding: (a) Aluminium-clad steel to aluminium-clad steel of different gauges; (b) aluminium-clad steel to mild steel; and (c) aluminium-clad steel to stainless steel. Data on cleaning procedure, electrode tip size, electrode pressure and current duration are presented.

Techniques for Welding Armour Plate. E. G. Biederman. (Welding, 1943, vol. 11, July, pp. 330-335). The author's paper on the welding of armour plate for tanks is reproduced (*see* p. 22 A).

The Weldability of (NE-8339) Manganese-Molybdenum Steel Piping. R. W. Emerson. (Welding Journal, 1943, vol. 22, Apr., pp. 170-S-178-S). As increasing quantities of National Emergency steels of the 8000-8500 series are being used in fabricated parts, the author carried out an investigation of the weldability of a steel representing this series; it contained carbon 0.33%, manganese 1.68%, silicon 0.28% and molybdenum 0.30%. His conclusions were: (1) The manganese and molybdenum in this steel promotes high hardenability which adversely affects the weldability. (2) The hardness obtained in the heat-affected zone of single-bead welds on specimens cut from tubing with a $\frac{7}{16}$ -in. wall, with no preheating, approaches that obtained by quenching in water. (3) Cracks will form in the heat-affected zone of all single-bead welds when the hardness exceeds 350 Brinell. (4) If this steel is welded with ferritic electrodes and without preheating, cracks will form in or close to the weld metal. (5) To obtain a good weld in this material it should be preheated to 500-700° F. and subsequently annealed. (6) Welds with a tensile strength of 44-47 tons per sq. in. and an elongation of 16-19% can be produced in this steel by normalising from 1600° F. after welding.

CLEANING AND PICKLING OF METALS

(Continued from pp. 121 A-122 A)

Blast Cleaning Greatly Facilitates Inspection of Bomb Casings. (Steel, 1943, vol. 112, May 24, pp. 86-88). A description is given of a machine for cleaning the inside and outside surfaces of large bomb-cases and shells. The outside is cleaned by steel shot projected by centrifugal force and the inside by shot in a stream of compressed air.

Industrial Metal Finishing. Part I. Aspects of the Corrosion of Metals and Alloys. Part II. Descaling and Pickling Processes. H. Silman. (Sheet Metal Industries, 1943, vol. 17, May, pp. 837-848, 855, 862; June, pp. 1015-1023; July, pp. 1199-1205; Aug., pp. 1385-1390). In the first part of this series the author considers the mechanism of the corrosion of ferrous and non-ferrous metals

and alloys referring to Evans' theory of differential aeration, the work of Vernon on the influence of dust and that of Hedges on protection by oxide films. In the second part the removal of scale by mechanical and chemical processes is dealt with; data on the consumption of compressed air in shot-blasting are presented. In centrifugal abrasive cleaning, the abrasive is allowed to fall on to a rotating wheel or series of impeller blades, from which it is projected centrifugally at high speed on to the parts to be cleaned; with careful design it is possible to control the direction of the abrasive very accurately. The composition of scale on steel is described and data on pickling in sulphuric acid and in hydrochloric acid are presented.

Immersion Heating—Determination of Flue Temperatures. H. C. McRae. (Iron and Steel Engineer, 1943, vol. 20, May, pp. 77-82). The author explains how to calculate the temperature of flue gases when designing immersion heaters for pickling tanks.

Reclaiming Waste Pickle Liquor. (Wire Industry, 1943, vol. 10, July, pp. 303-304). Some of the patented processes for reclaiming waste pickle liquors are reviewed. The use of continuous pH-value recorders and of submerged combustion burners for obtaining concentrated solutions has simplified some of the older methods of recovering hydrochloric acid and sulphuric acid. In war-time there is an adequate demand for both hydrochloric acid and ferrous sulphate, but in peace-time the demand for these two products may not be sufficiently balanced to make recovery an economic success.

COATING OF METALS

(Continued from pp. 122 A-126 A)

Hot-Dip Galvanising Technique. Part IX. The Spelter Bath. G. Robinson. (Wire Industry, 1943, vol. 10, May, p. 198). Conclusion of a series of articles (*see* p. 27 A). The author points out that the temperature of a galvanising kettle at which there is least dross formation is about 425° C. Where heavily coated wire is produced, 430-440° C. is recommended for No. 8 S.W.G. (standard wire gauge) and 440-470° C. for lighter gauges down to No. 18 S.W.G.

Conserving Critical Elements in Heat-Treating Equipment. H. S. Ingham. (Steel, 1943, vol. 112, Feb. 15, pp. 94-96). The author describes a method of coating steel with aluminium and treating the coating so as to protect the steel from the effects of heat. This is known as the Metcolising process. It has been found advantageous to make annealing covers and cyanide salt containers of carbon steel coated in this way in place of steel alloyed with chromium and nickel. The steel to be coated is first shot-blasted and then sprayed with about 1½ oz. of molten aluminium per square foot. A sealing solution is next painted on and the part is finally heat-

treated at about 1450° F. for 40 min. When heat is first applied to the coated steel, the aluminium melts and some of it is absorbed into the steel; the sealing coat prevents oxidation of the aluminium for a limited time, but when the sealing coat is finally burnt through, the aluminium is oxidised. The final coating consists of an outer skin of aluminium oxide, a thin layer of almost pure aluminium and a layer of iron-aluminium alloy of graded composition becoming higher in iron at increasing depth.

Chemical Surface Treatments for Steel. F. C. Hirdler, jun. (Monthly Review of the American Electroplaters' Society, 1943, vol. 30, June, pp. 502-512). **Phosphate and Oxide Treatments for Steel.** F. C. Hirdler, jun. (Iron Age, 1943, vol. 151, June 3, pp. 61-62, 128). The author gives a brief description of the phosphatising process for giving steel a protective coating. He recommends that, after treatment in the phosphate solution and rinsing, the steel should be dipped for about 1 min. in a 0.5-1.0% chromic acid solution at 180-200° F.; this kills any of the former solution which may still be on the steel and also increases the corrosion resistance of the coating.

Rust-Inhibiting Wax Coatings. W. Bridgeman. (Steel, 1943, vol. 112, Apr. 5, pp. 122, 155-156). The author points out that sprayed or brushed-on wax coatings are being increasingly used in the United States to protect finished and semi-finished parts from corrosion. The process is simple and inexpensive and has many advantages over oil and grease coatings.

The Development of the Hot Spraying of Powdered Materials. W. E. Ballard. (Chemistry and Industry, 1943, vol. 62, May 22, pp. 190-194). The author reviews the principal patents relating to the spraying of powdered metals, shellac and synthetic resins through a flame or zone of heated gases with the object of forming a coating.

Metal Spray Now Extended to All Flat and Irregular Surfaces. C. K. Wilson. (Steel, 1943, vol. 112, May 10, pp. 98-100). The author describes the "Fuse-Bond" process of preparing metal surfaces of any shape for metal spraying. This has already been described by W. C. Reid (*see* p. 29 A).

Relation of Hydrogen to Adherence of Sheet-Steel Enamels. W. A. Deringer. (Journal of the American Ceramic Society, 1943, vol. 26, May, pp. 151-159). The author describes experiments to determine the cause of the difference in the adherence of enamel coatings on steel sheet and on copper. The poor adherence of enamel (unless it contains cobalt oxide or nickel oxide) on steel sheet is due to the evolution of hydrogen at the metal-enamel interface as the steel cools. Some oxidising agent, such as ferrous oxide, is necessary to oxidise the hydrogen at the interface. The cobalt or nickel oxide may serve as an oxygen carrier to maintain an iron oxide layer at the interface, and this in turn reacts with the hydrogen to form water.

Acid Resistance and Technical Control in an Enamelling Plant. W. Montgomery. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 69, Apr. 8, pp. 279-283; Apr. 15, pp. 299-303; Apr. 22, pp. 329-332, 334; Apr. 29, pp. 353-354). The author describes the plant and processes for the preparation and application of enamel to steel and cast iron. The subject is dealt with in the following sections: (1) Composition of the base metal; (2) the type and construction of furnaces for fusing coatings on large vessels; (3) control of enamel mixes, milling times and temperatures; (4) testing enamels with the mobilometer and other instruments; (5) the glass lining of cast-iron vessels; (6) foundry practice and the composition of the iron; and (7) the effect of copper in cast iron on the adherence of enamel. The conclusions reached from some tests on the value of copper in cast iron for enamelling are: (1) The fluidity of the metal is increased, and this partly balances the lack of phosphorus in enamelling iron; (2) a refinement of the graphite structure gives pressure tightness and inhibits gas formation during firing, as, by virtue of the smaller graphite flakes, less oxidation and formation of the oxides of carbon can take place at the enamel-metal interface; (3) the eutectoid point occurs at a lower temperature when copper is present in cast iron, and shorter annealing times are necessary to complete the carbide breakdown; and (4) the copper-oxide skin controls the degree of surface oxidation of the iron at, and under, firing temperatures and gives a stronger grip to the ground coat.

Concentricity. E. F. Hansen. (Wire and Wire Products, 1943, vol. 18, Mar., pp. 170-171). When enamelled steel or copper wire is used for electrical purposes it is important that the thickness of the enamel film is uniform all round the wire. The author describes an instrument for rapidly testing the concentricity of 7-in. samples of wire. Wire 0.025-0.065 in. in dia. with an enamel film 0.001-0.006 in. thick can be tested.

PROPERTIES AND TESTS

(Continued from pp. 126 A-131 A)

Compression Testing of Cast Iron. W. L. Collins. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 111-113). This paper constitutes an appendix by Sub-Committee XI. on Methods of Testing of the A.S.T.M. Committee A-3 on Cast Iron. The author describes a useful and reliable method of compression testing that has been used satisfactorily at Illinois University. Details are given of the specimens and the compression tool with which the axial load is applied.

Progress Report on the Effect of Size of Specimen on Fatigue Strength of Three Types of Steel. H. F. Moore and D. Morkovin.

(Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 145-153). Tests have been carried out at the University of Illinois under the auspices of the A.S.T.M. Research Committee on Fatigue of Metals on specimens of two plain carbon steels (carbon 0.20% and 0.35% respectively) and one heat-treated chromium-molybdenum steel. Five different sizes of specimen turned down from 3- or 3½-in. dia. bars were used, the test diameters being $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{7}{8}$ or 1 in., and 1½, or 1¾, or 2 in. The tests were made in rotating cantilever machines. The maximum effect on the endurance limit attributable to size occurred with the 0.20% carbon steel. The endurance limit decreased with increasing size up to about $\frac{1}{2}$ in. in dia. Above this size the endurance limit remained fairly constant.

Factors Affecting the Influence of Nitriding on Fatigue Strength. W. E. Bardgett. (Metal Treatment, 1943, vol. 10, Summer Issue, pp. 87-101). The author reports the results of investigations of the effects of case hardness, case depth, degree of cleanness, stress concentration and corrosive influences on the fatigue strength of nitrided specimens of chromium-molybdenum steels. Because of compressive stresses in the nitrided case, nitriding increases the limiting fatigue stress. The effect of increasing the tensile strength by heat treatment is to diminish the effect of the nitrided case in raising the limiting fatigue stress; this increase is very much greater in notched than in plain specimens. The effect on the limiting fatigue strength of increasing the time of nitriding at 590° C. from 7 to 16 hr., thereby increasing the case depth from 0.0155 to 0.020 in., is negligible, but lowering the nitriding temperature to increase the hardness without alteration in case depth results in a decrease in the value for the limiting fatigue stress. The stress distribution and intensity of the junction between a nitrided and an un-nitrided surface do not appreciably affect the limiting fatigue stress of the un-nitrided portion. Inclusions, even of the size and quantity found in normal clean steel, appear to have a quite marked lowering effect on the limiting fatigue strength of nitrided specimens. Tests on the effects of notches on nitrided steels indicated that: (a) Provided that the stress gradient and/or stress concentration are insufficient to cause failure to commence from the surface of a nitrided specimen, the decrease in limiting fatigue stress with increase in stress concentration will be less than that of an un-nitrided steel. (b) If the stress gradient and/or stress concentration are such that failure commences from the surface of the nitrided specimens, the decrease in limiting fatigue stress with increase in stress concentration is greater than that of an un-nitrided steel, but the limiting fatigue stress of the nitrided steel is still appreciably higher than that of the un-nitrided steel. This was the case with the specimens of nitrided and un-nitrided steel used by C. G. Williams and J. S. Brown (see Journ. I. and S.I., 1942, No. II., p. 184 A). (c) The occurrence of a fracture from the surface of a nitrided specimen does not necessarily indicate a low limiting fatigue strength; con-

sequently notch sensitivity, as measured by the loss in fatigue strength due to a notch, may be low in a specimen showing fracture commencing from the surface, as was the case with specimens adopted in the author's tests.

Evaluation of Fatigue Damage of Steel by Supplementary Tension-Impact Tests. J. A. Kies and W. L. Holshouser. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 556-564). The authors examine the merits of tension-impact testing as a means of studying the changes occurring in steel during repeated stressing in the unsafe range before cracks start. Unnotched specimens were subjected to tensile-fatigue tests in a Haigh machine in the unsafe range and then subjected to tension-impact tests at room temperature and at -33°C . No appreciable loss in tension-impact resistance, or elongation during impact, resulting from prior repeated overstress in fatigue in the pre-crack stage were observed except for cases where the mean tensile stress and stress amplitude were high enough to cause permanent sets of more than 0.01 in. during fatigue stressing. Such conditions are improbable in service and would be easily detected. In cases where even the smallest detectable fatigue crack had formed before the tension-impact test there was usually a substantial loss in the tension-impact resistance. The fatigue crack had to be of easily detectable size before there was any adverse effect on the tension-impact resistance at -33°C .

The Notch Sensitivity of Alloyed Cast Irons Subjected to Repeated and Static Loads. W. L. Collins and J. O. Smith. (Proceedings of the American Society for Testing Materials, 1942, vol. 22, pp. 639-656). The authors investigated the notch-sensitivity of four different cast irons, namely, a low-alloy grey iron, a high-strength nickel-molybdenum iron, and inoculated iron and a high-nickel austenitic iron. In bending, torsional and tensile fatigue tests the low-alloy grey iron was relatively insensitive to notching, but with increasing static tensile strength of all irons the notch sensitivity to repeated loading increased. This tendency was less pronounced with the inoculated iron than with the others. All four classes of iron were insensitive to notching under static tensile, compressive and torsional loads.

An Investigation of the Static Notched Bar Behavior of Steel with Reference to Tri-Axial Stress and the Technical Cohesive Strength. O. H. Henry and J. G. Farmer. (Welding Journal, 1943, vol. 22, Apr., pp. 150-S-162-S). After reviewing the literature on the technical cohesive strength with special reference to the work of Kuntze, the authors report the results of an investigation of the effect of circumferential notches on the tensile strength of steel S.A.E. 6115, which is a low-alloy chromium-vanadium steel. Their conclusions were: (1) The effect of a circumferential notch on an axially loaded tension specimen is to decrease the percentage elongation and the percentage reduction of area, to increase the

ultimate tensile strength and the breaking stress and to decrease the work required to fracture the bar. (2) The ultimate strength of steel S.A.E. 6115 increases linearly with the depth of notch and the sharpness of the notch angle; the breaking stress also increases with notch sharpness, but not linearly; the ultimate tensile strength and the breaking stress approach each other with decreasing notch angle. (3) The character of the fracture of this steel in the normalised and stress-relieved state changes from ductile to brittle with decreasing notch angle at constant notch depth, but there is no sharp line of demarcation between the two types of fracture. (4) The linear relationship of tensile strength to notch depth and to notch angle as derived by Kuntze appears to apply to steel S.A.E. 6115.

The Influence of the Combination of Principal Stresses in Fatigue of Metals. D. J. McAdam, jun. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 576-592). The author discusses the relation between the three-dimensional diagram representing the influence of the combination of principal stresses on the technical cohesion limit of metals. (See Journ. I. and S.I., 1942, No. II., p. 184 A).

The Hardness Testing of Metals and Alloys. J. W. Donaldson. (Metallurgia, 1943, vol. 28, May, pp. 3-9). The author reviews methods of hardness testing and modifications which have been developed to meet special conditions, and considers hardness comparison scales. Details are given of the Brinell, Vickers, Rockwell, Monotron, Shore and Herbert methods of hardness testing. The Monotron and Herbert methods are not so well known as the others. The former is a static test using as an indenter a sphere 0.75 in. in dia.; the hardness is expressed by the load in kilogrammes required to make an impression 0.045 mm. deep and 0.33 mm. in dia. In the Herbert pendulum hardness tester use is made of the alteration in the time of swing of the pendulum by change of the centre of oscillation when a spherical-shaped diamond indenter, which is the point of support of the pendulum, moves in the grooves made by itself. It is useful for testing small specimens and thin materials.

Hardness Conversion Relationships. R. H. Heyer. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 708-721). The author studies the relationship between the results obtained when making Brinell and Vickers hardness tests on ingot iron, a variety of steels and several non-ferrous alloys. The tendency of some metals to flow under load in hardness tests makes it imperative to control the time of load application. Vickers hardness test results are comparable with Brinell results obtained with a $\frac{1}{16}$ -in. dia. ball when the ratio of the diameter of the Brinell impression to that of the ball is about 0.375. In the Vickers/Rockwell-B conversion relationship, the work-hardening capacity of a material has a very marked influence at hardness values below about 65 Rockwell B.

The Hardenability of Steel. A. J. K. Honeyman and J. Glen. (Journal of the West of Scotland Iron and Steel Institute, 1942-43, vol. 50, Part V., pp. 45-53). The authors explain how the following factors affect the hardenability of a steel: (1) The quenching medium and the method of quenching; (2) the shape and mass of the steel; and (3) its composition and method of manufacture. They review the Shepherd P.F. test, the Burns and Riegels test, Grossmann's method of evaluating hardenability and the severity of a given quench, and the Jominy end-quench test. The Shepherd test was developed in order to eliminate the occurrence of soft spots in tool steels. As a control test Shepherd took a series of $\frac{3}{4}$ -in. dia. bars of the same steel, heated them to different predetermined temperatures and quenched them in brine under standard conditions. The bars were then fractured and one half polished and etched to show the depth of the hardened zone. The remaining fractured half of the specimen was compared with a series of standards and served as a measure of the grain size of the steel. The Burns and Riegels test is an extension of the Shepherd test to include steels down to 0.1% of carbon. Grossmann's procedure has been explained in previous papers (see Journ. I. and S.I., 1940, No. II., p. 61 A and 1941, No. I., p. 58 A).

How to Use the Jominy End-Quench Test. G. Van Dyke. (Steel, 1943, vol. 112, May 17, pp. 106-110). The author describes the equipment and procedure for making the Jominy end-quench hardenability test. Among the tables of test data presented is one showing the rates of cooling of a 1-in. dia. specimen at increasing distances from the quenched end. Test results are quoted which prove the reliability of the test for predicting the hardness and tensile properties of heat-treated bars.

Properties of Hardened Steels. J. E. Erb. (Iron Age, 1943, vol. 151, May 27, pp. 39-47). The author reviews the literature on the properties of case-hardened steels and compares the mechanical properties of three types of hardened steels, namely, case-hardened steels with a soft core, hardened steels with a semi-hard core and through-hardened steels. The first type is least sensitive to notches, and the third type should be applied only for parts, such as bearing balls, which are subjected to compressive loads beyond the capacity of the other two types.

Temper Brittleness and Long-Time Heat Embrittlement. D. W. Rudorff. (Metallurgia, 1943, vol. 28, May, pp. 24-28). The author presents an abridged English translation of a report by E. Maurer, O. H. Wilms and H. Kiessler of their investigation of the tendency to temper brittleness and hot brittleness of 56 unalloyed and low-alloy steels. (See Journ. I and S.I., 1942, No. II., p. 32 A).

The Absolute Measurement of the Energy Loss in a Single Strip of Sheet Iron or Steel under Alternating Magnetization. W. E. Shenk. (Proceedings of the American Society of Testing Materials, 1942, vol. 42, pp. 595-618). Steel sheet for electrical purposes is rated

chiefly by the energy loss under cyclic magnetisation. A method is described which evaluates accurately this important characteristic in a simple manner in terms of absolute electrical measurements. It lends itself to power-loss measurement in whole sheets as well as in small specimens.

Steel Conductors for Transmission and Distribution of Electric Power. F. M. Crapo. (Wire and Wire Products, 1943, vol. 18, Apr., pp. 215-220, 244-246). The author discusses the use of steel wire for transmitting alternating current. The meaning of the hysteresis loop is explained, and the mechanical and electrical properties of a medium-carbon steel wire specially developed for high-tension alternating-current transmission are given. The wire is made in No. 4 and No. 6 gauges. Conductors of this steel wire are being used for a 44,000-V. three-phase transmission line, 35 miles long, in Utah.

Some Creep Studies on Cupola Malleable Cast Iron. J. J. Kanter and G. Guarnieri. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 659-667). The authors report the results of creep tests at temperatures in the 600-1000° F. range on specimens of white malleable cast iron. The creep strength at 800° F. was two-thirds that of silicon-killed carbon steel. The results indicated that a working stress of 5600 lb. per sq. in. at 775° F. is justified for this material; this value is several times the present limit imposed for this iron at a service temperature of 450° F.

Hydrogen and Nitrogen as Causes of Gassiness in Ferrous Castings. C. A. Zapffe and C. E. Sims. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-26). The amount of gas in iron and steel is a function of the hydrogen content and the changes in the solubility of hydrogen in the metal which take place during solidification. Hydrogen is introduced into the liquid metal by means of carriers, the most common of which is moisture. Bubbles of hydrogen can form only when nucleating centres are present. Austenitic steels are less liable to contain gas bubbles because hydrogen is more soluble in them than in ferritic steels. The addition of deoxidisers tends to increase the absorption of hydrogen. In exceptional cases, confined mostly to alloy-steel making, nitrogen may be the cause of "gassy" steel and "bleeding." Excessive absorption of nitrogen is much more easily attained when solid nitrides (*e.g.*, high-nitrogen ferro-chromium) are added to the melt, than when the metal is exposed to gaseous nitrogen; in such cases the nitrogen may be stabilised by adding a nitride-forming element such as titanium.

A Study of the Chemical, Physical and Mechanical Properties of Permanent Mold Grey Iron. R. Schneidewind and E. C. Hoenicke. (Proceedings of the American Society for Testing Materials, 1942, vol. 22, pp. 622-634). The authors report on an investigation of the properties of bars up to 2 in. in dia. of grey cast iron cast in water-

cooled and air-cooled metal moulds. The bars were annealed to give a structure of ferrite and graphite. The section size had a marked effect on some of the properties, the tensile strength of $\frac{1}{2}$ -in. bars being more than twice that of 2-in. bars; the compressive strengths of these two sizes were 124,300 and 99,800 lb. per sq. in. respectively.

Effects of Superheating, Pouring Temperatures and Micro-structure on the Elastic Properties of Some Plain and Alloy Cast Irons. A. I. Krynitsky and C. M. Saeger, jun. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 451-486). (See Journ. I. and S.I., 1942, No. II., p. 31 A.)

The Effect of Heat Treatment on Physical Properties of Some Common Irons Used in Oil-Field Equipment. E. R. Starkweather. (American Foundrymen's Association, Apr., 1943, Preprint No. 43-22). The author presents and discusses the results of tensile and hardness tests on four types of iron used for castings in oil-pumping machinery. The four irons contained total carbon 3.17-3.28% with silicon and manganese respectively at 1.29% and 0.74%, 1.45% and 0.56%, 1.59% and 0.60%, and 2.07% and 0.45%. They were hardened by quenching in oil from 1550° to 1600° F. and tempered at temperatures in the 800-1100° F. range. The tensile strengths of the bars was increased by 20-40% by the heat treatment as compared with those in the as-cast state. The strength of the softest iron was practically unaffected by changes in the tempering temperature, that of the other three irons also remained unchanged after tempering at temperatures up to 1100° F., but it decreased at higher temperatures.

Substituting Malleable and High Strength Iron. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, May, pp. 27-28). Some particulars are given of savings in copper and tin which have been affected in certain parts of naval and field-gun mountings by making them of either malleable cast iron or high-strength cast iron.

Foundry Metallurgy in the Castings Industry. J. W. Bolton. (American Foundrymen's Association, First Annual Foundation Lecture, Apr., 1943, Preprint No. 43-31). The author reviews progress in the castings industry dealing with the subject under the following headings: (1) Grey iron; (2) cast steel; (3) malleable cast iron; (4) non-ferrous metals excluding light alloys; (5) light alloys; (6) some principles in technology; (7) foundry metallurgy, the castings industry and the machine age; and (8) planned metallurgical progress. He suggests the directions in which further research would be valuable. Reference is made to the work of Montgomery and Urban which showed the tremendous differences in the creep strength of cast steel from the same heat and with fairly similar acceptance test results at room temperatures. Specimens of a welding quality molybdenum steel were heat-treated in different ways to produce four different structures, namely, coarse-grained acicular (transition product between pearlite-ferrite and martensite),

coarse-grained pearlite-ferrite, fine-grained acicular and fine-grained pearlite-ferrite. The creep rates calculated to 100,000 hr. under a load of 12,000 lb. per sq. in. at 950° F. in the period from 500 to 20,000 hr. were 1%, 3.5%, 7.5% and 48% respectively for the above four structures.

Here is an Explanation of how to Use Heat-Treated Carbon Steel Bolts. A. E. R. Peterka. (Steel, 1943, vol. 112, May 10, pp. 86-90, 135). The author quotes the results of tests to show that the strength of heat-treated carbon-steel bolts is often greater than that of alloy-steel bolts of the same or larger size.

Comparative Quality of Converter Cast Steel. C. E. Sims and F. B. Dahle. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 532-550). This paper, which deals with the mechanical properties of cast steel, has been published previously under the title "Converter Cast Steel Will Meet Requirements" (see Journ. I. and S.I., 1943, No. I., p. 60 A.).

Mechanical Properties of NE, S.A.E. and Other Hardened Steels. W. G. Patton. (Metal Progress, 1943, vol. 43, May, pp. 726-733). The author presents and discusses charts showing the relationship between the tensile strength and other properties of low-alloy steels including many NE and S.A.E. steels. As reflected by tensile tests on fully hardened steels, the apparent properties of low-alloy steels are subject to some fluctuation, regardless of composition. The variation from heat to heat for any one steel may amount to from $\pm 5\%$ to $\pm 10\%$, depending upon its hardness and the type of test.

National Emergency Steels ; NE 1300 Series. (Metal Progress, 1943, vol. 43, May, pp. 711-715). Data on the mechanical properties and hardenability of NE 1300 series of steels are presented and discussed. These steels contained 1.60-1.90% of manganese and up to 0.60% of carbon.

User Report No. 13 on Experience with NE (National Emergency) Alloy Steels in Aircraft Engines. M. Young and H. H. Hanink. (Society of Automotive Engineers : Steel, 1943, vol. 112, Apr. 26, pp. 84, 126-131). The authors give details of the composition and properties of AMS steels (Aircraft Material Specifications) which have been selected from the National Emergency steels for use in aero-engine construction.

National Emergency Steels. A. G. Zima. (American Society for Metals : Canadian Mining and Metallurgical Bulletin, 1943, May, pp. 140-153). The author gives tables of the compositions of National Emergency steels containing various combinations of different amounts of such elements as silicon, manganese, chromium, nickel and molybdenum, and discusses their hardenability, weldability, machinability and forging properties.

Leaded Manganese-Molybdenum Steel. T. Swinden. (Iron and Steel Institute, 1943, this Journal, Section I). Tests were carried out on material from a non-leaded and a leaded ingot of manganese-molybdenum steel in order to determine the effect of

lead (0.19%) on the mechanical properties, including the machinability. The leaded steel had a slightly coarser inherent grain size and less depth-hardenability than the non-leaded steel. The properties measured in the tensile test at room temperature were similar for the two steels in the form of flat and round bars. The notched-bar impact toughness of the leaded steel at room temperature was rather less than that of the non-leaded steel. At elevated temperatures the maximum-stress values of both steels were similar, but the ductility, as measured by elongation and reduction of area, was lower in the case of the leaded steel, particularly in the transverse direction. The Izod impact values of the leaded steel also were lower at elevated temperatures. The Barr-Bardgett creep-stress values of the two steels at 500° C. were identical, whilst no significant difference was shown by the figures for damping capacity. When treated to a tensile strength of 65 tons per sq. in. the fatigue ratio and notch sensitivity (rotary bending) of the two steels were similar. When treated to the lower tensile strength of about 55 tons per sq. in. the non-leaded steel had a higher fatigue ratio (rotating cantilever) and slightly greater notch sensitivity than the leaded steel. The fatigue ratio (direct stress) of the non-leaded steel compared with the leaded steel was slightly higher when treated to 65 tons per sq. in. and slightly lower when treated to about 55 tons per sq. in. The machinability of the leaded steel was markedly superior to that of the non-leaded steel.

Machinable 1.5 Per Cent and 2.0 Per Cent Chromium Cast Irons to Resist Deterioration at High Temperatures. C. O. Burgess and A. E. Shrubbsall. (Transactions of the American Foundrymen's Association, 1942, vol. 50, Dec., pp. 405-442). The authors describe a method of improving the machinability of cast iron containing 1.5-2.0% of chromium and a study of the heat-resistance properties of irons containing up to 2% of chromium. It was found that irons containing 1.5-2.0% of chromium which are normally white and unmachinable could be effectively softened by additions of graphitisers of the silicon-manganese-zirconium type without materially deteriorating their resistance to oxidation. The rate of oxidation at 800° C. of a 1.5%-chromium cast iron is only about one-fifth of that of an unalloyed iron. Increasing the chromium content causes the scale on heated cast iron to become denser. A concentration of chromium and silicon at the scale-metal interface of heated cast iron appears to occur. The appearance and analysis of the scale are not affected by graphitising additions. The growth of cast iron is markedly decreased by chromium additions; with 1.5% of chromium, only very slight growth occurs after heating for 516 hr. at 800° C., and with 2% of chromium the growth is negligible. Graphitised irons show slightly less growth than ungraphitised irons of similar chromium content.

The Physical Properties of Steel Wire as Affected by Variations in the Drawing Operations. H. J. Godfrey. (Proceedings of the

American Society for Testing Materials, 1942, vol. 42, pp. 513-526). See Journ. I. and S.I., 1943, No. I., p. 211 A.

Steels for Railway Rolling Stock. C. Dinsdale. (Engineer, 1943, vol. 175, June 18, p. 483). The author presents a comprehensive table of the composition and properties of the high-tensile low-alloy steels used by British and foreign railways for the construction of wagons and passenger coaches, and gives some examples of the saving in tare weight which have been effected in the United States by their use.

New Laboratories of the British Cast-Iron Research Association. (Metallurgia, 1943, vol. 28, June, pp. 67-70). **B.C.I.R.A. New Premises.** (Iron and Steel, 1943, vol. 16, July, pp. 472-474). A brief description is given of the organisation and research facilities at the new headquarters of the British Cast-Iron Research Association at Bordesley Hall, near Birmingham. The Association is organised in three main sections, the library and information bureau, the research department and the development department. The last two departments are aided by several laboratories, a machine shop and an experimental foundry.

Our Research Laboratories. (Welding Journal, 1943, vol. 22, Apr., pp. 145-S-149-S). An illustrated description is given of the electric welding research facilities at the Rensselaer Polytechnic Institute. The new welding laboratory was established in 1937. The premises include photographic, radiographic, spectrographic and mechanical testing departments. Instruments for the measurement of factors influencing the quality of spot and flash welds have been developed at this laboratory.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 131 A-134 A)

The Training of the Young Metallurgist. D. G. P. Paterson. (Sheet Metal Industries, 1943, vol. 17, Feb., pp. 253-256; Mar., pp. 431-434, 438; Apr., pp. 614-622; May, pp. 805-808; June, pp. 989-992; July, pp. 1163-1168, 1176; Aug., pp. 1349-1354). Continuation of a series of articles (see Journ. I. and S.I., 1943, No. I., p. 132 A). The author gives brief explanations and descriptions of metallurgical theory and practice which are important in the training of the metallurgist.

A Versatile Metallographic Polishing Process. Mildred Ferguson. (Metal Progress, 1943, vol. 43, May, pp. 743-744). An outline is given of the procedure at the Westinghouse Research Laboratories for polishing a wide variety of materials including carbon brushes, metals and glass-metal seals. In one step of the procedure, ordinary paraffin discs (melting point 55° C.) and an abrasive suspended in soap solution are used.

A Rapid Gamma-Ray Inspection Technique. R. C. Woods. (Metals and Alloys, 1943, vol. 17, Apr., pp. 764-766). The author gives details of a gamma-ray inspection technique designed to reduce the exposure time. The film is made up with a calcium-tungstate screen immediately behind it and front and back lead screens in addition. With a front lead screen 0.005 in. thick the customary exposure times can be reduced by about 85%. The gain in contrast by using a single calcium-tungstate screen is so marked that overdevelopment in potassium iodide developer is not necessary.

Radiography of Welds and Weldments. R. E. Lorentz, jun. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1046-1062). The author reviews developments since 1936 in the art of radiography as applied to welds. New fine-grained, high-contrast films have come into use which greatly improve the detail on the pictures obtained. The trend towards longer film lengths for special cases is discussed.

A Million-Volt Portable Radiographic X-Ray Unit. E. E. Charlton and W. F. Westendorp. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1088-1098). The authors describe a million-volt portable X-ray unit of small dimensions and light weight. Its principal features are the multi-section X-ray tube, the coreless resonance transformer and the Freon gas insulation.

High-Voltage X-Rays in the Boiler Shop. O. R. Carpenter. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1101-1108). The author discusses the experience obtained in the use of a million-volt X-ray equipment at the Baberton Works of the Babcock and Wilcox Company. The installation of this equipment necessitated a radical change in the X-ray technique. A special fine-grained direct-exposure film was developed for the purpose, and the use of lead foil screens in conjunction with it obviates the necessity for Bucky grids and calcium-tungstate screens and permits the standardisation of X-ray technique.

The Gamma-Ray Radiography of Welded High Pressure Power Plant Piping. R. W. Emerson. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1111-1129). The author describes the equipment required and the procedure for obtaining gamma-ray pictures of circumferential and longitudinal welds in steel tubes. To test the effect of size of the radium source, distance from source to film, metal thickness and type of film, gamma-ray radiographs were obtained of a test block in which three series of holes $\frac{1}{16}$, $\frac{1}{8}$ and $\frac{3}{16}$ in. in dia. respectively, were drilled; the hole depths varied from 0.010 to 0.100 in. in steps of 0.010 in. A radium source of 25 mg. was superior to one of 100 mg. for short source-to-film distances, but offered little advantage when this distance was increased beyond 6 in.

An Investigation of the Apparatus Used in Radium Radiography. L. W. Ball and D. R. Draper. (Proceedings of the Ameri-

can Society for Testing Materials, 1942, vol. 42, pp. 1134-1143). As a guide to radiographers in the selection and setting up of apparatus the authors discuss how variations in four factors affect the results obtained. These factors are: (1) The size of the gamma-ray source; (2) scattered radiation caused by the walls of the room and other objects; (3) the cassette containing the films and screens; and (4) the photographic equipment, comprising the film, solutions and viewing lamps.

An Exposure Meter for X-Ray Radiography. H. Friedman and A. L. Christenson. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1145-1153). The authors describe an X-ray exposure meter developed at the Naval Research Laboratory for use with a 220-kV. X-ray installation.

Equivalent Penetrameters in Radiographic Testing. R. J. Schier and G. E. Doan. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 1166-1168). The authors discuss the possibility of using penetrameters next to the film, on the outside of steel tubes of such small diameter that it is difficult to place it near the radium source inside the tube. The thickness of these penetrameters to make them equivalent to those specified in the code of the American Society of Mechanical Engineers was determined experimentally.

A Study of Austenitic Grain Growth in Medium-Carbon Steels. J. H. Whiteley. (Iron and Steel Institute, 1943, this Journal, Section I). A detailed investigation has been made of austenitic grain growth in unstrained medium-carbon steels throughout the whole of the temperature range between the Ac_1 and the solidus point. To ascertain the positions of the austenite grain boundaries at the temperature of heating the ferrite precipitation method was used, since it was found to be reliable and without any restriction in application. To record the grain sizes thus disclosed the counting method was largely employed, in which the average number of grains present in 10 sq. in. at a magnification of 100 is taken as the standard of comparison. The steels examined fall for the most part into two categories, *viz.*, coarse-grained and fine-grained, the latter type being produced by the addition of 1 lb. of aluminium per ton of metal in the ladle. Intermediate types could not be obtained simply by adding lesser amounts of aluminium. Eight interdependent factors were found to influence growth, *viz.*: Temperature, length and rate of heating; initial grain size, hot-work and the aluminium content of the steel; the rate of cooling from the solidus to 1200° C. and the state of the carbide. The manganese content of the steel may be yet another factor. With so many possible combinations an exhaustive examination of the subject was impracticable, but from the work done the conclusion may be drawn that any particular grain size formed by heat treatment in a given medium-carbon steel is the result of the concerted action of these various factors. It is shown that grain refinement takes place almost entirely at the Ac_1

transformation and is completed during the passage through the critical range. In the coarse-grained steels the rate of growth then steadily increased with the temperature of heating, and below about 1100°C . a state of virtual stability was eventually reached. In the fine-grained steels a remarkable halt in grain development occurred almost immediately after the refinement. Below 900°C . this period of inactivity was indefinitely long, and, as a consequence, the steel was fine-grained in character. Above 900°C . the halt became progressively shorter, but at any one temperature its actual duration could be varied widely by changing the rate of heating, the initial grain size and other factors. When once the halt was passed mixed grain sizes began to appear, consisting of large dominant grains embedded in small ones. Dominant growth of a relatively few grains was an effect also observed in coarse-grained steels, but the small grains did not remain so inactive. As the temperature was raised the mixed grain sizes gradually disappeared. After refinement by forging, a smaller grain size grew in coarse-grained steels at temperatures up to at least 1000°C . than after an equal refinement by heat treatment, and it is shown that the disparity was not due to differences between the banded heterogeneity or to the distribution of the inclusions. Hot-work seemed to be the cause. In fine-grained steels this factor was not so much in evidence, owing to the mixed grain sizes which were formed in the temperature range where it operated. The production of a coarse-grained steel was found to depend on the rate of cooling from either the liquid or solid condition to 1200°C . Unless the rate was fairly slow the steel was fine-grained in character. In the absence of manganese the change to the coarse-grained type could not be induced even by a very slow cooling. The state of the carbide had an important influence both on the extent of growth and on the length of the halt. Complete spheroidisation of the pearlite greatly minimised growth, especially in fine-grained steels. The effects of quenching and of quenching and tempering on growth were not the same as those of spheroidisation. Shortly after the first halt in well-tempered pieces with a large initial grain size a second halt occurred which persisted for a long while to above 1050°C . Attempts were made to convert solid coarse-grained steels into fine-grained by diffusing aluminium into them, but the results were inconclusive.

Second Report on Metallographic Examination of 18 per Cent Chromium 8 per Cent Nickel Steel. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 134-143). This is a Report by Sub-Committee VI. on Metallography of the A.S.T.M. Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys. The purpose of the work was to study the nature of the material precipitated at the grain boundaries of 18/8 steel when it is heat-treated in a manner which renders it liable to intergranular attack. Samples of the steel were annealed and held for one week at 550° , 650° , 750° and 850°C ., respectively. They were

examined by five different laboratories after etching with sodium cyanide and with Murakami's reagent. Sodium cyanide is more positive and reliable than Murakami's reagent for detecting precipitated carbides, but neither reagent reveals a difference in microstructure commensurate with the relative susceptibility to intergranular corrosion. The nature of the precipitated material was not ascertained, but it was established that there is no correlation between the amount observed in the grain boundaries and the susceptibility to intergranular corrosion. There were indications that when the intergranular precipitation is thin and continuous the susceptibility to corrosion is much higher than when it takes the form of larger and separate particles. X-ray diffraction patterns of residues of samples treated in a solution of hydrochloric acid and potassium copper chloride were obtained. The residue from the sample annealed at 850° C. consisted of well crystallised Cr_4C with traces of Cr_2N and austenite. The residue from the 750° C. specimen was a mixture of Cr_4C and austenite. The amount of Cr_4C in the residue from the 650° C. specimen was much lower than that in the 750° C. specimen, and only a trace was present in the residue from the 550° C. specimen.

CORROSION OF IRON AND STEEL

(Continued from pp. 134 A-137 A)

Air-Heater Corrosion in Boiler Plant. (British Coal Utilisation Research Association, Biennial Report, 1940-41, pp. 37-39). An account is given of some experiments to determine the mechanism of the corrosion of tubes in air-heaters for power-station boilers. A study of the conditions under which SO_2 may be oxidised after leaving the combustion chamber showed conclusively that there is no homogeneous gas-phase oxidation of SO_2 to SO_3 under experimental conditions comparable (as regards temperature and time of contact) with those in a boiler. The oxidation of SO_2 in solution is promoted by catalytic agents such as iron or manganese, and it proceeds most rapidly if the SO_2 is present as sulphite ions. It may be concluded that SO_2 must be combined with or converted into some other compound before it can be oxidised. Experiments with the solids in flue gases are proceeding.

Fatigue Tests as a Means of Evaluating Corrosion Damage of Sheet Metals. W. H. Mutchler and J. A. Kies. (Proceedings of the American Society for Testing Materials, 1942, vol. 42, pp. 568-572). Bending fatigue tests in Krouse-type machines were made on specimens of stainless steel sheet before and after corrosion by prolonged exposure to sea air, and to air and sea water alternately by the action of the tides. The rate of corrosion, as measured by the loss in

fatigue strength, was relatively rapid at first, but exposure for 2½ years after the first six months had very little effect on the corrosion damage. For the same period of exposure the corrosion damage was greater in sea air than in sea water and air alternately.

Zinc Yellow in the Inhibition of Corrosion-Fatigue of Steel in Sodium Chloride Solution. C. G. Fink, W. D. Turner and G. T. Paul. (Electrochemical Society, 1943, Preprint No. 83-13). The authors report the results of corrosion fatigue tests on specimens of cold-drawn 0.29% carbon steel wire, 0.0371 in. in dia., which were bent in an arc and revolved while immersed in a sodium-chloride solution, a Kenyon fatigue machine being used (*see* Journ. I. and S.I., 1935, No. II., p. 486). The object was to test the corrosion-inhibiting action of zinc yellow. Zinc yellow gave better protection than the equivalent concentration of chromate in the form of the potassium salt. The addition of zinc ions to a sodium-chloride solution reduced the rate of corrosion appreciably. The authors believe that the zinc ion reacts with the hydroxide ion liberated by the corrosion reaction at the cathode, covering the latter with a film of insoluble zinc hydroxide which interferes with the ability of oxygen to reach the cathode. When the supply of oxygen to the cathode is obstructed, the ability of reactions to take place at the anode is diminished. Raising the zinc ion concentration to 10 times its concentration in zinc yellow solution and adding chromate was less effective than using zinc yellow alone. The effect of chromate ions on sodium chloride solutions is very dependent on temperature and the fatigue stress range.

Caustic Embrittlement Research Brings Results. J. H. Walker. (Mechanical Engineering, 1942, vol. 64, Dec., pp. 891-893). The author summarises the results of research conducted by the United States Bureau of Mines on the caustic embrittlement of boiler material. The necessary chemical conditions for embrittlement to occur are the presence of sodium hydroxide in appreciable amounts, the absence of inhibiting agents and, at the higher pressures, the presence of silica. The effectiveness of sodium sulphate as an inhibitor has not been satisfactorily confirmed. Lignin-containing materials, such as waste sulphite liquor, and tannin materials, particularly quebracho, are satisfactory inhibitors. Quebracho is stable and is effective in boilers operating at pressures up to 700 lb. per sq. in. To obtain satisfactory results the ratio of quebracho to total alkalinity should be not less than 0.4 to 1. Sodium nitrate is stable at pressures up to 400 lb. per sq. in. and is an effective inhibitor if the ratio of sodium nitrate to total alkalinity is not less than 0.4 to 1.

MINERAL RESOURCES

(Continued from p. 65 ▲)

Marampa—A Mountain of Ore. (Iron and Steel, 1943, vol. 10, May 20, pp. 347–351). A brief account is given of the iron-ore mountain of Marampa and the ore-shipping facilities at Pepel in Sierra Leone. Under the crust of crude red rock ore the grey powder ore is almost pure. Garatt-type articulated locomotives haul 36-truck trains with 1000 tons of ore down the 52-mile track to Pepel, where there is a jetty with an endless conveyor capable of loading 1500 tons of ore per hr. into ships. The maintenance and repairs, including lathe work, casting, forging, welding and riveting, are all done by native labour.

The Steep Rock Iron-Ore Deposits. (Canadian Mining Journal, 1943, vol. 64, July, pp. 437–444). An account is given of the discovery, exploration and plans for developing the iron-ore beds of Steep Rock Lake, Ontario. The conclusions reached are: (1) These deposits are of exceptionally good grade and constitute an iron range of importance equal to that of any other range in the Lake Superior region, except the Mesaba Range; (2) it will be possible to deliver this ore at Lower Lake ports at a competitive price; (3) the conditions are such that it will be possible to mine an average of at least 2,000,000 tons of ore per annum for many decades; (4) the known supply of hard ore of comparable grade in the Lake Superior region is very limited, so that a ready market for the maximum tonnage of Steep Rock ore that can be mined seems to be assured.

Titaniferous Adirondack Ores Being Reworked. F. J. Oliver. (Iron Age, 1942, vol. 149, Mar. 5, pp. 53–59). The author gives an account of the discovery in 1826 and the subsequent intermittent exploitation of a vast titaniferous iron ore bed at Sandford Hill in the upper reaches of the Hudson River in the Adirondack Mountains. The ore contains about 16% of TiO_2 , and it is now being worked by the National Lead Co. The programme of operation calls for the mining of 5500 tons of ore per day, and the mill under construction is to produce 800 tons of ilmenite containing about 48% of TiO_2 for use in paint manufacture. There will be stock-piled about 1800 tons per day of magnetite concentrates containing about 89% of Fe_3O_4 , 10% of TiO_2 and 1% of silicon. The difficulty of dealing with the magnetite is not one of smelting, but of transport on a large scale from this remote region.

Preliminary Studies Necessary for Making a Depth Survey of the Iron Ore Beds of Vizcaya. A. del Valle de Lersundi. (Notas y Comunicaciones del Instituto Geológico y Minero de España, 1942, No. 10, pp. 3–10). (In Spanish). Information is given on the geology of the iron ore beds in the Bilbao region.

ORES—MINING AND TREATMENT

(Continued from p. 100 A)

Fine-Screening Investigations—I. S. Mörtzell and P. V. Villner. (Jernkontorets Annaler, 1943, vol. 127, No. 4, pp. 98-128). (In Swedish). The authors give an account of the work of a committee set up in 1939 by Jernkontoret to study the fundamentals of fine-screening. A number of factors used in screen-analysis calculations are defined; thus, the "screening limit" is the narrow range of grain size of the unscreened material which, after screening, is found in equal proportions above the screen and below it. Ore concentrates from Rudgruvan, near Fagersta, and from Vintjärn were used on vibrating screens measuring 1330×550 mm. Screens of three different meshes were used with holes 0.30×0.30 mm., 0.22×0.22 mm. and 0.15×0.15 mm., respectively, and the slope of the screen was kept at 20° in all the tests. The rate at which the screen became choked was found to depend mainly on the rate of loading. After only 6 hr. the choking was so great that the screening efficiency was reduced by 50%. The screening limit was also reduced by the choking. Tests were made by moving a vibrating wooden comb over the material on the screen at 10-min. intervals; this effectively cleaned the screen, *e.g.*, the screening efficiency was just as good after 4 hr. as after 30 min. A method of making reliable and comparable screening tests was also developed. The test data are presented in numerous tables and graphs.

Rotary Kilns for Agglomerating Ores. S. G. Thyrré. (Steel, 1943, vol. 113, July 5, pp. 116-118, 131). Under war-time conditions in the United States a number of rotary kilns in the cement industry are idle, and experiments are being conducted to see whether these could be used for sintering iron ore. Application for patenting the "agglomerating method" has been made. The ore to be sintered is mixed with an "agglomerating agent" made by grinding a mixture of iron ore and limestone in a mill. The ore and the agglomerating agent are fed into the rotary kiln and, as the mixture passes through, it reaches a temperature above the softening point of the latter, but below the fusion point of the ore. The iron-ore particles are thus bound together to form nodules. In most kilns trouble due to the formation of rings on the lining has not been experienced, and, when rings have formed, they were of a light and spongy nature and easily removed.

Sinter—Its Development and Use—The Process—Plant Design. C. E. Agnew. (Steel, 1943, vol. 112, May 31, pp. 84-88, 102; June 7, pp. 119-120, 154, 158; June 14, pp. 112-114, 139-143; June 21, pp. 103-104, 129-132). The author traces the history of pig-iron manufacture in the United States, and shows that at the present time more and more attention is being given to sintering.

There now exist plants with a total capacity of 13,000,000 tons of sinter per annum. The sintering of ore on a large scale near the mines is advocated. If the chemical elements are present in the sinter mix in proportions which will form the structure-strengthening iron silicates and the mix is properly fused, the production of hard sinter is inevitable. If there are insufficient base elements other than iron present to balance the amount of silica in the mix, the excess silica will satisfy itself with iron alone to form the silicate fayalite, Fe_2SiO_4 ; this silicate has an exceptional strengthening effect on the sinter. A good standard to aim at is to have a natural silica content of about 5–6% balanced with base elements other than iron in the ratio of 1.5 to 1.0. By feeding lime to a sintering mix in the form CaO instead of CaCO_3 , a self-fluxing sinter could be produced, but the cost of burnt lime prohibits its use for this purpose. Where earthy ores are screened the usual practice is to transfer the oversize particles to the furnace trestle and charge them into the furnace direct. An increase in sinter production might be obtained by crushing the oversize particles and re-introducing them into the mix so as to open up the bed of material to make an easier passage for the waste gas. Some design features of the Agnew sintering machine are described. In this an endless train of cast pallets slide over stationary rollers; this permits the installation of any desired permanent-pressure lubrication system to all rollers, and water-cooling to all roller shafts. With stationary rollers the seal joint is at the side of the pallet above the rollers. The sides of the seal are readily accessible and easily maintained. The application of a gas-washer to a sintering plant appears to be quite feasible, and would greatly increase the exhaust fan efficiency.

REFRACTORY MATERIALS

(Continued from pp. 143 A–144 A)

The Ternary System $\text{MgO}-\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$. W. T. Wilde and W. J. Rees. (Transactions of the British Ceramic Society, 1943, vol. 42, July, pp. 123–155). The authors report on a study of magnesia, alumina and chromic oxide, and their reaction products, at temperatures up to fusion. Their conclusions were: (1) The binary system $\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$ shows complete solid solution, with no complicating factors. The precise position of the solidus and liquidus phase boundaries remain to be determined, but no confirmation has been obtained of the abnormally high melting point of 2135°C . given by Bunting for chromic oxide. The suggestion that the more usually observed melting point of $2060-2080^\circ \text{C}$. is due to the formation of a lower oxide has been disproved by the demonstration that when reduction occurs, chromium metal is obtained in equi-

librium with the sesquioxide. (2) The binary system $\text{MgO-Al}_2\text{O}_3$ possesses only one compound, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, which can take a considerable amount of alumina into solid solution at high temperatures. No evidence has been obtained of any solid solution of magnesia in $\text{MgO} \cdot \text{Al}_2\text{O}_3$. It has been shown that alumina is precipitated from spinel-alumina solid solution when cooling is slow. (3) The binary system $\text{MgO-Cr}_2\text{O}_3$ possesses one compound, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$. So far no conclusive evidence has been obtained for the suggestion that this compound may take either magnesia or chromic oxide into solid solution. It has been shown that whatever solid solution does occur, it is negligible in furnace-cooled specimens. The evidence for the existence of a compound $4\text{MgO} \cdot \text{Cr}_2\text{O}_3$ has been reviewed, and on the basis of a thorough X-ray investigation of this part of the system it has been concluded that no stable compound of this formula exists. (4) In the high-magnesia portion of the ternary system the lattice dimensions of the spinel compounds appear to depend solely on the relative proportions of chromic oxide and aluminium oxide present. In the low-magnesia portion, the proportion of magnesia present also has a slight effect. The diffuse nature of the pattern of the rhombohedral phase in the low-magnesia portion of the system suggests that precipitation in the solid-state may be taking place as in the $\text{MgO-Al}_2\text{O}_3$ binary system, but this cannot yet be taken as fully proved. A complete series of solid solutions is formed between $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and $\text{MgO} \cdot \text{Cr}_2\text{O}_3$. The series is not completely regular and suggestions have been put forward to explain the irregularities. No ternary compounds are formed.

An Investigation into a Rapid Method of Assessing the Resistance of Refractory Materials to Disintegration by Carbon Monoxide. F. H. Clews, H. M. Richardson and G. R. Rigby. (Transactions of the British Ceramic Society, 1943, vol. 42, June, pp. 105-110). When carbon monoxide is passed over crushed firebrick contained in a fused silica tube at 450°C . the amount of carbon dioxide produced can be used to measure the extent of the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ and to assess the resistance of the brick to disintegration by carbon deposition. The results obtained in this way on eleven firebrick cylindrical samples for prolonged periods to the action of carbon monoxide. As the basis for a quick test to assess resistance to carbon-monoxide disintegration, it is suggested that: (1) A half-brick or piece of similar size is crushed to pass an 8-mesh sieve, and a 75-g. sample obtained by quartering; (2) carbon monoxide, freed from carbon dioxide and oxygen, and saturated with water at room temperature, is passed over the sample in a silica tube at 450°C . at the rate of 1 litre per hr.; (3) materials which result in the formation of more than 0.1 g. of carbon dioxide, i.e., 0.13% of the weight of the sample, in the 4-hr. period commencing 30 min. after the temperature has reached 450°C . may be regarded as liable to disintegration by carbon monoxide.

Refractories for Desulphurizing Ladles. C. E. Bales and D. R. Smith. (*Industrial Heating*, 1943, vol. 10, May, pp. 728-736; June, pp. 886-894). The authors point out the difficulty of obtaining a satisfactory refractory material which will resist the attack of slags obtained when desulphurising iron with soda ash. A good plastic material has been developed by mixing a highly calcined Kentucky flint clay with a high-grade ceramic bonding clay; its good performance is ascribed to the formation of mullite crystals on the surface. The technique for applying this material to vessels of different shape is described in detail.

PRODUCTION OF IRON

(Continued from pp. 145 A-146 A)

Moves Blast Furnace to Mexico. R. R. Hetz. (*Steel*, 1943, vol. 112, June 28, pp. 98-100, 119, 120). The author gives an account of how a blast-furnace and some of the auxiliary plant was dismantled at St. Louis on the Mississippi and re-erected at Monclova in Mexico. The furnace had not been used since 1923, and at its new position it will be able to supply iron for the shipyards on the Gulf of Mexico.

The Blowing of Blast Furnaces. W. Goldsbrough and S. G. Throssell. (*British Steelmaker*, 1943, vol. 9, Aug., pp. 341-349; Sept., pp. 399-407). The authors present a summary of the important factors relative to blast-furnace blowing which have appeared in the literature, and add some of their own conclusions. Data on the characteristics of atmospheric air are given, and these are followed by explanations, with examples, of methods of calculating: (1) The amount of air to be supplied to the blast-furnace; (2) the work of compression; (3) the heat of compression; (4) the blast pressure at the tuyeres; (5) loss of pressure due to friction in blast mains; and (6) the saving effected in blowing costs by reducing the loss of blast pressure between the blower and the horse-shoe main.

The Manufacture of Sponge Iron. C. F. Ramseyer. (*Engineers' Society of Western Pennsylvania: Blast Furnace and Steel Plant*, 1943, vol. 31, May, pp. 516-520; June, pp. 649-653). The author reviews ancient and modern processes of making sponge iron. A plant designed by Julian Madaras is being erected in Texas; this uses treated natural gas as a reducing agent; it is a batch process carried out at about 1800° F., and the reducing gas is supplied at a pressure pulsating between 35 and 65 lb. per sq. in. A plant designed by T. W. Hornsey has been operating for some time at Lorain, Ohio. This comprises three rotary kilns; in the first, the ore, mixed with reducing coal, is preheated; it is reduced in the

second and cooled in the third kiln. There are six factors which now have an important bearing on sponge-iron manufacture in America. These are: (1) The immense size of the magnetite ore beds of the Eastern States; (2) the ability to concentrate these ores to a product equal to the finest Swedish ore; (3) the ability of the modern wet magnetic concentrating plant to handle fine material down to 200 mesh; (4) the fact that hydrogen is a very much more active reducing agent than carbon monoxide at temperatures below 1500° F.; (5) the great advances in the development of large-scale equipment for producing hydrogen from coke, petroleum products, or natural gas; and (6) the development of automatic equipment for controlling temperature, the flow of fluids, chemical reactions generally and combustion in particular. These factors have made possible the Brassert low-temperature gaseous reduction process as carried out in the Brassert-Cape-Herreshoff reduction unit at a temperature of 1100° F. This process is not a direct competitor of the blast-furnace, but is looked upon as an auxiliary. By the parallel use of the two processes, many of the available ores could be exploited to better advantage than is possible by either process alone. Fine ores are very desirable in the Brassert process, as the velocity of the reducing gas rising through the beds in the reducing furnace can be kept low by removing the spent gas from each different hearth. The reoxidation of the finely divided, chemically active sponge iron is prevented by briquetting the material into a solid melting stock while it is still hot and in the reducing atmosphere. The first plant of this type is under construction at the works of the Republic Steel Corporation.

Charcoal Pig Iron. R. H. Sweetser. (Iron Age, 1943, vol. 152, July 1, pp. 43-47). The author reviews the available information on the reasons why charcoal iron is stronger than coke iron of the same analysis. The only feasible explanation appears to be that the graphite flakes in the former are smaller and the ferrite has better continuity. The production of charcoal iron in the United States has risen from 43,600 tons in 1938 to 104,700 tons in 1942. The possibility of reforestation to grow hardwood in the vicinity of suitable ores is considered.

Development and Manufacture of Silvery Pig Iron. B. H. Booth. (Industrial Heating, 1943, vol. 10, Feb., pp. 220-230; Mar., pp. 376-386; June, pp. 844-850). The author describes the development in the United States of high-silicon silvery pig iron and how it is produced by the Jackson Iron and Steel Co., Jackson, Ohio. (See p. 6 A).

Smelting of Vanadium-Bearing Titaniferous Sinter. (Iron Age, 1943, vol. 151, June 24, pp. 59, 131). A brief account is given of the results obtained in an investigation by the United States Bureau of Mines of the smelting of sinter made from the titaniferous magnetite ore found in New York State. A recovery in the metal of 87.3% of the vanadium in the sinter was obtained when operating

the 6-ton experimental blast-furnace on burdens of iron ore and titaniferous sinter containing 11.1% of titania and 0.26% of vanadium; about 4% of the vanadium was lost in the slag. With up to 25% of sinter in the burden, no difficulties were experienced. With burdens composed of sinter 53% and high-grade hematite 47%, the slag averaged 16.8% of titanium. In general, when the slag contained more than 15% of titania there were difficulties in the hearth, in the combustion zones and in the bosh of the furnace.

The Desulphurisation of Pig Iron with Acid Slags. W. Oelsen and H. Maetz. (*Archiv für das Eisenhüttenwesen*, 1943, vol. 16, Feb., pp. 283–298). The authors report on laboratory tests they carried out to study the theories put forward by R. Durrer, H. Hellbrügge and B. Marinček (*see Journ. I. and S.I.*, 1942, No. I., p. 175 A) and by R. Durrer and B. Marinček (*see Journ. I. and S.I.*, 1943, No. I., p. 4 A), who have previously investigated the desulphurisation of iron with acid slags with lime/silica ratios in the 0.49–0.62 range. The results obtained, using melts in graphite crucibles, lead to the conclusion that the formation of gaseous silicon sulphide is responsible for only a small proportion of the strong desulphurising effect which the acid slag has at 1700° C. The greater part of the desulphurising is effected by the initially acid slag only after the iron has taken up a large amount of silicon (over 4%, which makes the iron of little use commercially) and the final slag has thus become less acid. The major portion of the sulphur, as a rule more than 70% of the total sulphur present, remains in the final slag after desulphurisation of the iron. Prolonging the reaction time increases the silicon content of the iron, thus increasing the basicity of the slag and causing the sulphur content of the iron to be reduced to a very low point. The proportion of sulphur removed in the gas phase, which may amount to up to 30% of the total sulphur, is quite small in comparison with that removed from the iron by the final slag. This slag may, for example, reduce the sulphur in the iron from 0.6% to 0.01%. Reducing the quantity of acid slag lowers the degree of desulphurisation considerably, but it must be remembered that decreasing the silicon in a small quantity of acid slag increases the basicity to a greater extent than with a large quantity of slag. Additions of titania to the acid slag at high temperature do not act as a flux, but increase the amount of silicon passing into the iron, thus making the slag more basic and improving the desulphurisation. Of the added titania, only a small proportion remains in the slag at the high temperatures in question and not much passes into the iron; it is probable that most of it remains on the crucible wall in the form of titanium carbide. The data obtained, which are presented in several tables and graphs, are in good agreement with observations made in blast-furnace practice.

FOUNDRY PRACTICE

(Continued from pp. 147 A–151 A)

Meeting the Raw Material Supply Position in Grey Iron Foundries. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, Aug., 12, pp. 299–302; Aug. 19, pp. 325–328). *See* p. 107 A.

Hints on Founding Low-Carbon Cast Iron. J. W. Nicholls. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, Aug. 12, pp. 309–310). The principal difficulty in making castings of low-carbon iron is due to the high solidification point and the greater freezing range. The tapping of dull metal can be caused by the bed coke being too low and/or insufficient coke split, and/or insufficient blast. Greater attention must be paid to mould drying. Runner bushes should be of dry sand or core sand, not green sand.

Tropenas Converter Practice. E. C. Pigott. (Metallurgia, 1943, vol. 28, June, pp. 81–83; July, pp. 139–143). After describing the development of the Tropenas converter, the author gives details of the design of a modern unit and its operation in conjunction with a cupola for the production of clean steel at a high temperature for castings.

The Continuous Production of Manganese Steel Castings from the Tropenas Converter. L. W. Bolton and J. Hill. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, Aug. 19, pp. 319–323; Aug. 26, pp. 347–351, 353). *See* p. 110 A.

Desulphurizing in Converter Steel Practice. G. S. Evans. (Metals and Alloys, 1942, vol. 16, July, pp. 80–81). The author gives some particulars of “Purite,” a form of fused soda ash cast in 2-lb. pigs, and describes the technique of using it for desulphurising metal prepared in the cupola from charges with a high proportion of steel. The desulphurised metal is then refined in a side-blown converter.

Hot Tear Formation in Steel Castings. C. W. Briggs. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 70, Aug. 5, pp. 277–282; Aug. 12, pp. 303–308). *See* p. 109 A.

REHEATING FURNACES

(Continued from p. 79 A)

The Modern Soaking Pit and Blooming Mill. T. J. Ess. (Iron and Steel Engineer, 1943, vol. 20, Apr., pp. B-19–B-79). The author presents a comprehensive review of modern soaking-pit and blooming-mill plant and practice in the United States. The soaking-pits

described include: (a) Reversing regenerative pits by the Rust Furnace Co.; (b) pits with top firing by the Surface Combustion Co.; (c) circular pits by the Salem Engineering Co.; (d) Amsler-Morton recuperative pits fired from a single burner in the middle of the floor; and (e) rectangular pits, by the Swindell-Dressler Corporation, fired with two gas or oil burners placed in opposite walls 3 ft. above the coke bed. The Isley control system for reversing regenerative pits is also described and data on heating times and fuel consumptions are given. A list of all the blooming mills in the United States shows that the sizes range up to 54 in. between centres of the mill pinions, with most of them between 34 and 46 in. Most of the roll-neck bearings are still of bronze with Babbitt-metal inserts. Some synthetic-resin bearings with fabric reinforcement are in use; this material has in some cases had a life equal to rolling 300,000 tons for the top rolls and up to 800,000 tons for the bottom rolls. Diagrams of many rolling-mill lay-outs and roll contours, as well as power-consumption curves, are given.

War Products Consultation: Heating of Heavy Forging Billets. (Metal Progress, 1943, vol. 43, May, pp. 724-725). Seven replies are presented to a request for advice on the heating of 25-in. square billets of 0.40% carbon steel for forging. The recommendations differ in detail, but are consistent in calling for a slow rate of heat input in the sub-critical temperature range.

FORGING, STAMPING AND DRAWING

(Continued from pp. 153 A-154 A)

Forging Die Design. J. Mueller. (Heat Treating and Forging, 1943, vol. 29, Apr., pp. 177-178; June, pp. 279-280). The author describes the design of dies for forging special T-pieces and ball and stem forgings for helve hammers.

Douglas Drop Hammer Technique. P. Stayboldt. (Iron Age, 1943, vol. 152, July 8, pp. 58-61). The author describes the pressing technique adopted at the Douglas aircraft factory, Long Beach, for shaping aircraft parts using Cecostamp drop hammers.

Forging High Traction Differential Pinions. R. J. Goldie. (American Society of Tool Engineers: Heat Treating and Forging, 1943, vol. 29, May, pp. 231-232, 250; June, p. 281). The author describes the development of forging dies for making differential gear bevel pinions which require no subsequent machining. The dies were made to fit a coining press of 2000 tons capacity making 80 strokes per min. The main difficulty was that the thin flash cooled so rapidly that the excess metal would not extrude as required, with the result that the die broke. This was overcome by leaving a depression in the back face of each tooth of sufficient size to absorb the metal displaced in the coining operation.

Forging Steel Turbine Blading. W. H. Lloyd. (Heat Treating and Forging, 1943, vol. 29, July, pp. 331-335, 345). The author describes the making of dies for turbine blades and the various stages in which they are forged out of an iron alloy containing 11.5-12.5% of chromium.

Substituting Steel for Brass in the Press Shop. (Sheet Metal Industries, 1943, vol. 18, Aug., pp. 1409-1413). Some details are given of the technical difficulties encountered and overcome in the making of steel shell cases at the Buick Motors Division of the General Motors Corporation.

Two-Stage Drawing of Cylindrical Cups. H. W. Swift. (Institution of Engineers and Shipbuilders in Scotland: Engineering, 1943, vol. 156, Aug. 13, pp. 137-140; Aug. 27, pp. 178-180; Sept. 3, pp. 199-200; Sept. 10, pp. 219-220; Sheet Metal Industries, 1943, vol. 17, June, pp. 995-1000, 1009; July, pp. 1179-1186, 1193; Aug., pp. 1365-1370, 1379; Sept., pp. 1547-1552). The author gives an account of research sponsored by the Institution of Automobile Engineers on the stresses involved in the two-stage drawing of cylindrical cups. The results of earlier work on the drawing of a cup in a single operation from a flat circular blank are reviewed. The effects of various re-drawing ratios following a fixed initial drawing ratio were studied experimentally. The punch load necessary to re-draw a given first-stage cup was found in all cases to increase as the re-drawing punch diameter was made less; the relationship between re-drawing load and punch diameter was not so clearly defined as in the initial draw, but it was in all cases approximately linear. The re-drawing load for a given re-drawing punch diameter increased with the initial blank diameter. During the first stage of the re-drawing operation a considerable thinning of the base of the cup accompanied the cupping process, while the portion of the walls which was being drawn down the taper of the die becomes thicker, and the outer rim, which had not yet commenced to draw, remained unchanged in thickness. The more severe the re-drawing operation, the greater was the thinning in those parts where thinning predominated and the greater was the thickening in the upper part of the walls where the higher re-drawing ratio was not compensated by subsequent tensile thinning. Investigations of the influence of interstage heat treatment led to the following conclusions: (1) Interstage annealing produced a definite improvement in re-drawing capacity in all the cases examined. (2) The greatest value of the combined drawing ratio was in each case obtained when the initial draw had been carried to the full capacity of the material. (3) The slope and setting of the re-drawing characteristic varied from one metal to another. (4) So far as two-stage performance was concerned, mild steel was less sensitive to the particular value of the first-stage drawing ratio than a metal like aluminium, which has a steeply sloping re-drawing characteristic.

ROLLING-MILL PRACTICE

(Continued from pp. 116 A-117 A)

Fundamental Investigations on the Cold and Hot Rolling of Metals. O. Emicko and K. H. Lucas. (*Zeitschrift für Metallkunde*, 1942, vol. 34, Feb., pp. 25-38; *Sheet Metal Industries*, 1943, vol. 17, Apr., pp. 611-613; May, pp. 800-804; June, pp. 979-987; July, pp. 1159-1162; Aug., pp. 1355-1359; Sept., pp. 1541-1544). This is an English translation from a German paper in which the authors present and discuss the results of about 1000 cold-rolling tests on lead, aluminium, two aluminium-copper-magnesium alloys, one aluminium-magnesium-manganese alloy, a 15%-nickel steel and a 5%-aluminium steel. Methods of determining the torque and roll pressures under different conditions are explained.

Mills and the Roll Designer. C. Elms. (*Iron and Steel Engineer*, 1943, vol. 20, June, pp. 41-46). The author describes the development of the modern rolling mill and the part played in this by the roll designer.

Bearing Surfaces. E. L. Hemingway. (*Iron and Steel Engineer*, 1943, vol. 20, May, pp. 53-58). In discussing the smoothness of bearing surfaces the author distinguishes between short-pitch and long-pitch defects. Grinding ridges form an example of short-pitch defects, and they can be detected by a profilometer or a Brush analyser. Long-pitch defects are caused by inaccuracies in the machine tool carrying the grinding wheel, and they cannot be detected by a profilometer. With white-metal bearings, loose particles become embedded in the soft metal and the bearing acts as a lap on the shaft. With harder bearing metal, such as bronze, the particles are not so deeply embedded, or they remain suspended in the oil and, in either case, scoring of the shaft is the result.

Additives in Petroleum Products. F. F. Musgrave. (*Iron and Steel Engineer*, 1943, vol. 20, May, pp. 40-44). The author discusses the functions of addition agents in petroleum-base lubricating oils. These include: (a) Those which increase the film strength, *e.g.*, chlorinated wax; (b) detergents, such as alkaline-earth alkyl phenates, which reduce the formation of sludge; (c) corrosion inhibitors, such as phosphorus esters; and (d) agents which increase "oiliness," *e.g.*, fatty acid esters.

The Vanderbijl Steel Works, Transvaal. (*Engineer*, 1943, vol. 176, July 2, p. 9). Some particulars are given of the stage now reached in the erection of the steelworks at Vanderbijl in the Transvaal. This plant will receive slabs from the Iscor works at Pretoria. The plant comprises a producer-gas-fired reheating furnace with a hearth 80 ft. by 18 ft. and a plate mill to be driven by a motor, developing 17,000 h.p. at peak loads, with all auxiliary machinery and equipment.

Electronic Control for Steel Mill Auxiliaries. J. H. Hopper. (Iron and Steel Engineer, 1943, vol. 20, June, pp. 62-71). After an explanation of the principles of thermionic valves in which the characteristics of the kenotron, pliotron, phanotron, thyatron and ignitron valves are pointed out, the author discusses their application to various forms of control in rolling mills.

What the Amplidyne Has Contributed to Reversing Mill Drives. C. B. Huston. (Blast Furnace and Steel Plant, 1943, vol. 31, June, pp. 654-658). The author discusses the use of amplidyne control for reversing mill drives. The advantages of this control include: (1) It permits the replacement of large contactors handling field currents of up to 300 amp. by small relays which handle only a fraction of one ampère; (2) it reduces the number of control devices by about 50%; (3) it provides accurate control of acceleration and deceleration; (4) it provides effective control of load limits, making available the maximum torque output of the motors at all times; and (5) it provides accurate balance of load between two or more machines operating in parallel, and the proper balance of torque and speed on the two units of a twin drive.

HEAT TREATMENT

(Continued from pp. 155 A-159 A)

What is the Future of Induction Heating in Heat Treating, Joining, Forging, Melting? F. W. Curtis. (American Society of Tool Engineers: Steel, 1943, vol. 112, May 31, pp. 76-78; June 14, pp. 117-120, 143; Machine Shop Magazine, 1943, vol. 4, July, pp. 76-79). The author points out the advantages of induction hardening. In a comparison of the costs of hardening gears it is shown that the induction hardening of a 0.45% carbon steel cost 43% less than carburising a 0.20% carbon steel even after including the extra cost of the high-carbon steel.

The Heat Treatment of Solid A.P. and S.A.P. Shot. (Steel, 1943, vol. 112, June 21, pp. 90-91, 125, 133). Three types of mass-production units for the heat treatment of solid armour-piercing and semi-armour-piercing shell are described. In the smaller units the shell travel round a circular furnace to an opening from which they are removed to the quenching tank with tongs by hand. In large units the shell are conveyed through the oil-bath to the tempering furnace on a conveyor which carries rows of eight cages, each cage holding a single shell nose downwards.

The Heat Treatment of High-Speed Steel. A. Linley. (Metallurgia, 1943, vol. 28, July, pp. 127-132). The author discusses the theory and practice of the heat treatment of the following high-speed steels: 14/4/1 and 18/4/1 tungsten-chromium-vanadium steel,

5%-cobalt steel, 10-12%-cobalt steel and 4-6%-molybdenum steel. The maximum hardness of 14/4/1 steel is obtained by quenching from about 1160° C., with molybdenum steel the quenching temperature is 1150-1250° C., and for the other three steels it is 1250° C. Suitable tempering temperatures for these five steels are: No. 1, 560-580° C.; No. 2, 580-620° C.; No. 3, 580-620° C.; No. 4, 600-625° C.; and No. 5, 550-580° C.

Heat Treatment of High-Speed Steel Tools. W. A. Schlegel. (Steel, 1943, vol. 112, June 28, pp. 106-109, 122-127). The author discusses the heat treatment of 18/4/1 tungsten-chromium-vanadium high-speed steel and two other types containing 4.50% and 8.50% of molybdenum respectively. Furnace atmospheres rich in carbon monoxide should be employed. The steel with 8.50% of molybdenum is liable to decarburise in an ordinary furnace atmosphere, but this can be prevented, or greatly reduced, by using carbon blocks or coating the steel with compounds having a borax or copper-oxide base. The two molybdenum steels show maximum secondary hardness when tempered at 1025-1050° F., whilst the 18/4/1 steel requires tempering at 1050-1075° F.

Automatic Heat Treating in a Jobbing Forge Shop. R. R. LaPelle. (Iron Age, 1943, vol. 151, June 17, pp. 52-53). The author describes the continuous heat-treatment plant installed by the General Drop Forge Co., Buffalo. This is designed to handle a wide variety of parts in trays. The furnace is fired with low-pressure gas burners staggered along both sides of the furnace and projecting into combustion chambers below the alloy-steel rails along which the trays are pushed.

Additional Notes on the Cold Treatment of Metals. (Iron Age, 1943, vol. 151, June 17, pp. 66-67). Some examples are given of the improved life of gauges obtained by chilling treatment at -120° F., or by alternate hot and cold treatment in boiling water and a refrigerating unit. (See p. 49 A).

Keeping Cool. P. H. Harris. (Machine Shop Magazine, 1943, vol. 4, May, pp. 41-43; June, pp. 49-52). The author discusses the fitting of metal parts in engineering assemblies by the shrinkage of the outer member and the expansion of the inner one. In many cases, particularly in the aircraft industry, it is advantageous to cool the inner part and a description of a portable refrigerator employing solidified carbon dioxide is given.

Salt Bath Heat Treatments for Emergency Steels. (Schweizer Archiv: Iron Age, 1943, vol. 151, June 24, pp. 60-62). A brief review is presented of German practice in the heat treatment, using electrically heated salt-bath furnaces, of chromium-manganese steels, which are used as substitutes for steels containing nickel.

Dry Cyaniding in the Production Heat Treat. L. L. Clark and C. H. Leland. (Heat Treating and Forging, 1943, vol. 29, June, pp. 295-300). The authors describe the dry-cyaniding process of case-hardening as practised by the Buick Division of General Motors

Corporation. Dry cyaniding is carried out by heating the parts in a furnace or muffle in an atmosphere of neutral producer gas, town gas or coke-oven gas to which anhydrous ammonia is added. When heated in a mixture of 90% of coke-oven gas with 10% of ammonia for 3 hr., the maximum content of nitrogen in the case was obtained after heating at 1400° F. and the amount decreased with increasing temperature; the carbon content was low at 1400° F. and increased to a maximum at about 1600° F. The continuous plant at the Buick works is operated at 1550° F. with about 700 cu. ft. of producer gas per hour to which are added 5 to 25 cu. ft. of propane and 50 to 150 cu. ft. of ammonia per hour according to the particular case requirements. Small parts are loaded with a shovel on to low-sided perforated trays and are pushed through the furnace; a case depth of 0.007 in. min. is obtained in 1½ to 2 hr. It is possible to shorten the time by using a greater proportion of ammonia and slow cooling.

Nitriding Tools in Liquid Salt Baths. G. W. Esau. (Steel, 1943, vol. 113, July 12, pp. 104-106). The author gives brief details of the nitriding of high-speed tool steel in liquid cyanide baths. The salt used has a melting point of 920° F. and the bath is operated at 1000-1200° F. The usual depth of case obtained is 0.001-0.002 in. after 30 to 90 min. immersion. Very high surface hardness is obtained and this has to be determined by a scratch test or by the Vickers method; for instance, after 30 min. immersion at 1050° F., a case depth of 0.0013 in. with a hardness (calculated from the Vickers reading) of Brinell 937 was obtained.

Machine for Hardening Steel Rings. (Engineering, 1943, vol. 156, Sept. 3, p. 187). **Shorter Patent Hardening Machine for Large Circular Tracks.** (Machinery, 1943, vol. 63, Aug. 19, pp. 218-219). A brief illustrated description is given of a Shorter flame-hardening machine for hardening the surface of rings from 1 ft. to 9 ft. 4 in. in dia. The machine consists of an electrically driven turntable with jigs to hold the ring in position, a push-button starting switch, automatic limit switches to stop the rotation where desired and brackets to hold the burner and quenching heads.

Making Surfaces Hard by Flame-Hardening. R. Gunnert. (Teknisk Tidskrift, 1943, vol. 73, May 22, pp. M45-M54). (In Swedish). The author gives a comprehensive account of the theory and practice of flame-hardening. The metallurgical effects and many types of burner heads and quenching equipment are described in detail and data on the consumption of oxygen and acetylene for different jobs are given.

Low Carbon Irons for Electrical Relays. A. Brookes. (Iron and Steel, 1943, vol. 16, Aug., pp. 527-530). A coke-fired furnace for heat-treating small iron parts of relays used in telephone installations was recently replaced by the latest design electric furnaces with automatic control and two ammonia crackers to supply the inert atmosphere. The initial results were that some of the annealed

batches were too brittle and their magnetic properties were inferior. Investigation established that the phenomenal brittleness of the low-carbon iron was due mainly to hydrogen penetration causing the cementite at the crystal faces to be reduced to spongy iron.

Metallurgical Control Through Calculated Hardenability. W. R. Patterson. (Iron Age, 1943, vol. 152, July 1, pp. 40-42, 130). The author explains some applications of Grossmann's hardenability calculations to the control of the heat treatment of steels of unfamiliar and varying analyses. Grossmann's procedure has been explained previously (*see* Journ. I. and S.I., 1940, No. II., p. 61 A, and 1941, No. I., p. 58 A).

Unusual Results Achieved with Controlled Atmosphere Hardening Furnace. G. E. Stedman. (Heat Treating and Forging, 1943, vol. 29, July, pp. 347-350). A shaker-hearth hardening furnace is described in which parts are heated in an atmosphere of cracked natural gas. The parts, hardened by quenching in oil, are particularly clean and free from scale.

WELDING AND CUTTING

(Continued from pp. 159 A-160 A)

Welding Low-Alloy High-Strength Steel. W. Spraragen and H. H. Chiswick. (Welding Journal, 1943, vol. 22, June, pp. 225-S-263-S). The authors review the literature from January 1, 1938, to January 1, 1941, on the welding of low-alloy high-strength steels.

Welding Wrought Iron, High Carbon Steel and Cast Steel. H. R. Morrison. (Welding Journal, 1943, vol. 22, June, pp. 418-420). The author makes recommendations on the procedure for oxy-acetylene welding wrought iron, high-carbon steel and cast steel.

Stainless Steel Aircraft Exhausts. H. A. Campbell. (Society of Automotive Engineers: Iron Age, 1943, vol. 151, June 24, pp. 56-58). The author discusses the prevention of cracks in welds in stainless steel exhaust pipes for aero-engines. Both titanium-stabilised and columbium-stabilised stainless steels are good materials for these exhaust pipes. The tendency towards brittleness and cracking increases as the borax and boric-anhydride constituents of the welding flux are increased. No bits of zinc alloy from any other source must be allowed to remain on the stainless steel during welding or annealing as this also causes cracks.

Arc Welding Dissimilar Metals. A. F. Davis. (Metals and Alloys, 1942, vol. 17, July, pp. 69-70). The author describes the technique for welding brass to steel, cast iron to steel, and high-manganese steel to low-carbon steel.

Arc Welded Blast Furnace. R. F. Fey. (Iron Age, 1943, vol. 151, June 24, pp. 48-55, 130). The author gives details of the

design of the joints and the welding procedure adopted in the erection of an all-welded blast-furnace and welded stoves at the works of the Weirton Steel Co. The erection was carried out with considerable saving in both cost and time as compared with riveted construction.

The Stress-Relieving and Normalising-Annealing of Welded Assemblies. E. Helin. *Teknisk Tidskrift*, 1943, vol. 73, July 17, pp. M69-M78). (In Swedish). The author presents and discusses the results of tensile tests on specimens of weld metal and welded joints in the as-welded, the stress-relieved and the normalised state. It is shown that in many cases stress-relieving, which is less expensive than normalising, provides adequate protection against the risk of cracking in welded assemblies.

Advantages and Limits of the Processes Used in Finishing Heat-Treatment of Welds. W. Zimm. (*Die Wärme: Sheet Metal Industries*, 1943, vol. 18, Sept., pp. 1614-1618, 1620). The author describes after-treatments for gas and electric welded joints. Hot-peening of oxy-acetylene welds is advocated, but this is not recommended for electric welds unless the hot-peening is followed by an annealing treatment. It is better to utilise the welding heat and carry out the peening while the temperature is above the A_{c_3} point than to allow the weld to cool and apply external heat afterwards.

Metallurgy of Spot Welding. H. Lawrence. (*Steel*, 1943, vol. 112, Mar. 29, pp. 100-103, 108). The author presents and discusses data on electrode size, mechanical pressure and area of weld obtained in the spot welding of steel sheets of different thickness.

Flame Cutting in Steel Plants. S. D. Baumer. (*Iron and Steel Engineer*, 1943, vol. 20, June, pp. 58-61). The author describes and illustrates some of the latest types of oxy-acetylene cutting apparatus used in steelworks. One of these is a machine with an oscillating head with which the width of cut may be as much as $1\frac{1}{2}$ in.; ingots up to 32 in. thick can be cut with it.

The Gas-Cutting Process and Its Effect on Steel. T. J. Palmer. (*Metallurgia*, 1943, vol. 28, June, pp. 73-76; July, pp. 108-110). After a brief explanation of the principles involved in the hand and machine oxy-acetylene cutting of steel, the author discusses its metallurgical effects. The carbon content is the most important single factor governing the degree of hardness produced near gas-cut edges. The limit of carbon which may be present if workable edges are to be retained after cutting is about 0.3%. With higher-carbon or alloy steels, preheating in the 300-500° C. range is necessary if machinable edges are to be left. The influence of the size of the cutting-oxygen orifice, the oxygen pressure and the speed of travel on the quality of cut obtained is described and illustrated.

Band Sawing Forgings. H. J. Chamberland. (*Heat Treating and Forging*, 1943, vol. 29, July, pp. 343-345). The author gives some examples of the advantageous use of the band saw in the trimming of forgings and the cutting of special shapes.

MACHINING

(Continued from pp. 86 A-88 A)

Machining Efficiency and Lead-Bearing Steels. (Journal of the Institution of Production Engineers, 1943, vol. 22, June, pp. 211-229). Empirical laws governing the relationship between factors affecting machining speeds and tool life, and the results of machining tests on lead-bearing steels are discussed. Schlesinger and others reported that there is some relation between the Brinell hardness of the steel being machined and its machinability index, but the author has found that this is not strictly valid and does not apply to cold-drawn steels which have work-hardened as a result of the drawing; nor does it apply to steels containing lead. Details of tests showing the excellent machinability of lead-bearing steels are given.

Standard Carbide Tips for Special Tools. P. W. Miller. (Iron Age, 1943, vol. 151, June 3, pp. 63-64). The author gives some examples of the saving in time and cost which can be achieved by using standard sizes of tungsten-carbide tips in tools of special design.

Extracting Oil from Swarf. (Machine Shop Magazine, 1943, vol. 4, July, pp. 56-58). A considerable amount of the cooling agents employed in machining operations is carried away with the swarf and in many machine shops its recovery is worth while. Illustrated descriptions are given of centrifuging machines and the transport equipment necessary for the efficient recovery of cooling agents from swarf.

Emulsions for Metal Working (First Communication). H. Stäger and H. Künzler. (Abteilung für industrielle Forschung des Instituts für technische Physik an der ETH, Zürich: Schweizer Archiv für angewandte Wissenschaft und Technik, 1943, vol. 9, Nos. 3 and 4). The authors study the factors affecting the efficiency of cooling agents, particularly emulsions, used in machining operations. These liquids have both a cooling and a lubricating action, and these two properties are very difficult to determine, as they cannot be treated separately. For a given cross-section of machining cut the temperature difference between dry and cooled cuts decreases with decreasing cutting temperatures or rate of cut. With low cutting speeds the lubricating power of the liquid used is mainly responsible for the quality of surface produced, but at high cutting speeds the cooling action is more important. The wetting power of a liquid is increased by decreasing its surface tension. The surface tension of water can be reduced by adding sodium laurate solution; such solutions are "surface-active" and they have different efficiencies which follow the Traube law. Whilst pure fatty acids follow this law, soaps do

not exactly conform to it. The surface activity of soap first increases with higher members of the homologous series, and then falls off; higher temperatures cause the maximum capillary activity to shift to the higher homologues. The inclination of the surface-tension/temperature curve will approach the horizontal, the more concentrated the solution and the higher the soap in the homologous series. Attempts have been made to obtain stable emulsions of mineral oils and water by using suitable emulsifiers. The action of the emulsifier depends on the ease with which the emulsion is formed, the stability of the emulsion, and the fineness or degree of dispersion of the emulsion; the fineness and the stability are the most desirable properties. Examples of stable and unstable emulsions are discussed and microphotographs of them are reproduced. In one case a flocculent precipitate of lime soap is seen. The use of an unsuitable emulsifier with water containing lime may give very unstable emulsions, owing to the concentration of the emulsifier being reduced by the formation of lime soap. The corrosion of metals during machining with an emulsion as cooling agent is a complicated phenomenon, because the corrosive agent consists of at least two phases and the interfaces in its system may act like diaphragms. To prevent rusting, attention must be paid not only to the composition of the emulsion, but also to its action. The concentration of an emulsion must be adjusted to the quality of the surface to be obtained if the necessary protection against corrosion is to be given. The interfacial tension in a liquid-liquid system, which governs the formation and stability of the emulsion, decreases with rising temperature. Emulsions should never be prepared at temperatures below 12°C . or above 40°C .; the method of blowing in steam should, therefore, not be used. Suitable emulsions have been developed which are entirely satisfactory as substitutes for fatty free-cutting oil and for mixtures of mineral oils with electrically treated mineral oils and fatty oils; the emulsions are such good lubricants that an excellent surface can be obtained when milling threads on chromium-nickel steel. Emulsions have also been substituted for rape oil used in the stamping of gear teeth; the quality of the metal surface is even improved and the consumption of the emulsion is much less than that of the rape oil. It is suggested that suitable emulsions could also be used to replace soaps and fatty oils for wire-drawing.

Surface Finishes on Machined Parts; Their Inspection and Comparison. W. Mikelson. (American Institute of Electrical Engineers: Steel, 1943, vol. 112, Jan. 25, pp. 62-67). The author describes the system adopted by the General Electric Co., Schenectady, for specifying surface finishes. The surface roughness characteristic is measured by the height in microinches (10^{-6} in.) of the irregularities. Ten degrees of roughness varying from 4 to 2000 microinches have been established and are shown on drawings by the symbols f^1 , f^2 , f^3 , &c. The various departments are supplied

with standard specimen panels with which the surface of parts in production are compared.

PROPERTIES AND TESTS

(Continued from pp. 163 A-172 A)

Dilatometric Equipment from the Lunkenheimer Co., Cincinnati. H. E. Montgomery and J. W. Bolton. (Metals and Alloys, 1942, vol. 16, July, pp. 52-55). The authors describe a dilatometer developed at the research laboratories of the Lunkenheimer Co., which combines accuracy with reasonable sensitivity and the advantages of direct reading on a chart. It has three ranges of expansion and contraction sensitivity. The specimen is heated by an electric furnace and the expansion is transmitted by a quartz rod to a sliding contact held in an Invar bracket; when contact is made, a solenoid puts one of the gear trains in operation in the recording unit and at the same time sets a Selsyn motor in motion causing a threaded contact to screw out and break the circuit; this in turn stops the solenoid from functioning and all the recording mechanism stops.

Recommended Procedure for the Impact Test for Cast Iron. (Foundry Trade Journal, 1943, vol. 70, July 22, pp. 239, 246). A Sub-Committee of the Technical Advisory Panel to the Directors for Iron Castings of the Ministry of Supply has been studying the impact testing of cast iron with a view to developing a standard procedure. The Sub-Committee is not yet able to put forward a test for standardisation, but it recommends a procedure the principal features of which are that the test should be carried out in the standard 120 ft.-lb. Izod impact machine using a 0.798-in. dia. plain specimen with no notch or groove and a striking height of 22 mm. measured from the top of the rear grip.

Notched Impact-Test Specimens for the Investigation of Steel at Low Temperatures. H. Bennek. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Feb., pp. 307-308). As it is extremely unlikely that the steels used for containers and chemical plant at low temperatures would ever be subjected to such impact stresses, or to such severe conditions as occur when impact tests are made on the German standard DVM specimen, the author carried out impact tests at temperatures from $+20^{\circ}$ to -180° C. on specimens of heat-treated chromium-manganese steel with notches varying from 50 to 2 mm. in width and from 3 to 4 mm. in depth. From the test results it is concluded that the DVM specimen is satisfactory for temperatures down to about -50° C., but for lower temperatures a shallower notch would be better; the notch suggested forms a semicircle with a radius of 4 mm.

Fatigue Failures in Common Machine Parts. J. O. Almen. (Metal Progress, 1943, vol. 43, May, pp. 737-740). The author cites some instances of the failure of steel parts due to fatigue and makes recommendations concerning them. The case of bolts subjected to cyclic stresses proves that, if the initial bolt tension is less than the maximum external load, the stress range under repeated loads is increased. A bolt or stud should be tightened to a load exceeding the maximum working load, thus reducing the fatigue stress range and prolonging the life of the bolt. Pre-stressing a bolt shank by peening, and pre-stressing the roots of threads by rolling, also increase the fatigue strength.

Improving Fatigue Strength of Machine Parts. J. O. Almen. (American Gear Manufacturers' Association: Iron Age, 1943, vol. 151, June 10, pp. 65-69, 125-131). The author points out that the surface of a fatigue-test specimen is always more vulnerable to fatigue than the deeper layers; this may be due to sub-microscopic notches or simply to the fact that the outer crystals are not supported on their outer surfaces. Pre-stressing to increase the fatigue strength can be done by peening, quenching or cold-working, but there is a critical limit to the amount of peening and cold-work above which the fatigue strength decreases. When machine polishing is done with abrasive paper, cloth wheels, or abrasive-covered felt wheels, high surface tension stresses which are detrimental to the fatigue strength may be induced. Pitting of gear teeth may occur when no load is transmitted, if the gears are running submerged in oil, because the oil is trapped between the teeth sometimes at extremely high pressure.

The Fatigue Strength of Cast Iron. A. Thum and C. Petersen. (Archiv für das Eisenhüttenwesen, 1943, vol. 16, Feb., pp. 309-312). The authors study the effect of the graphitic carbon in cast iron on its tensile and fatigue strength. The rate at which the tensile strength of cast iron falls with increasing graphitic carbon is small at first because the resistance to necking is high, but with increasing graphitic carbon the tensile strength falls more rapidly because the graphite then permits greater deformation up to a certain maximum point. With still more graphite, the particles interlock and this decreases the rate at which the strength of the already reduced section of the iron is lowered. On the other hand, the fatigue strength (under cycles of tension and compression) depends chiefly on the notch effect of the graphite particles, which is very great even with little graphite present, so that the fatigue strength decreases quite slowly with increasing graphitic carbon. A method is developed for determining the fatigue strength (tension-compression) of cast iron from the tensile strength and Brinell hardness.

Fatigue Strength of Butt Welds in Ordinary Bridge Steel. (Welding Journal, 1943, vol. 22, May, pp. 189-S-211-S). This paper constitutes Report No. 3 of Committee F of the Welding Research

Council of the Engineering Foundation of Illinois University. A Progress Report on fatigue tests of welded joints in structural steel plates has already been published (*see* Journ. I. and S.I., 1941, No. II., p. 135 A). In the present paper an account of tensile-fatigue tests on butt welds in specimens of mild steel $5 \times \frac{7}{8}$ in. in section is given. From the data obtained the weld stresses which similar joints would resist up to 100,000 and 2,000,000 cycles were calculated under two sets of conditions: (a) Fairly ideal conditions, using skilled welders for horizontal welding; and (b) commercially butt-welded in accordance with the American Welding Society Specifications for Welded Highway and Railway Bridges which cover welding in shop or field in any position. The results obtained were:

	No. of Cycles of Repeated Stresses (zero to maximum tension)		No. of Cycles of Reversed Stresses (zero mean stress)	
	100,000	2,000,000	100,000	2,000,000
(a) Min. fatigue strength	32,000	22,100	21,400	13,300
(b) "Dependable" fatigue strength				
	27,000	18,000	16,500	11,000

The Determination of the Effect of Various Types of Weld Metals on the Internal Damping Characteristics of Steel Specimens. O. H. Henry, R. R. Feitl and J. A. Falcon. (*Welding Journal*, 1943, vol. 22, June, pp. 266-S-269-S). After considering the general theory of damping and explaining the terms "absolute damping capacity" and "specific damping capacity," the authors describe tests in which the effects of welds using filler metal of bronze, monel metal, nickel and nickel steel for mild steel plate on the specific damping capacity were investigated. Pieces of $\frac{7}{8}$ -in. steel plate were welded together and specimens were cut 12 in. long so that the joint was at the centre of an 8-in. length turned to $\frac{3}{4}$ in. in dia. The specimens were firmly clamped in a vertical position at the lower end by a block attached to a heavy steel foundation plate; a massive horizontal bar was clamped rigidly to the upper end of the specimen 1 in. from the top, and electro-magnets were placed near the ends of this bar. The strength of the magnets was adjusted so as to produce the desired stress in the specimen. On breaking the magnet coil circuit the specimen oscillated freely and a recording of the movement was obtained by a pen attached to one end of the horizontal bar. All the curves obtained followed the general shape of the curve for the unwelded specimen; the specimens welded with bronze and monel metal had a slightly higher specific damping capacity than that of the unwelded specimen. Calculations showed that the damping at the weld-metal/base-metal interface was exceedingly small and that, in general, the welding had little effect on the damping capacity of the specimens.

The End-Quench Test. J. Winning. (*Mechanical World*, 1943, vol. 113, May 28, pp. 573-575). The author describes the Jominy

end-quench test and jigs for making it and for making the diamond-pyramid hardness survey along the specimen. Tables are given showing typical results as well as the rates of cooling of bars 1, 2, 3 and 4 in. in dia., quenched in oil and in water, at positions on the surface, at the centre and at half the radius. Examples are given of the application of these data to predict the hardenability of a steel.

Metallurgical Aspects of Wear. (Machinery, vol. 63, Aug. 19, pp. 211-213). The types of wear known as scoring, galling, abrasion and pitting are described. It is possible to obtain a hard and uniform metal surface, as indicated by production hardness tests, and yet, judging from the hardness of individual crystals, as measured with a microhardness machine, the same surface is most inconsistent. The very low hardness of siliconised steel parts considered in conjunction with their excellent wear-resisting properties casts doubt on the popular belief that high hardness is essential for good wear-resistance. It would appear that the degree of superfinish can be exploited only in those conditions where the surface, by virtue of its microstructural homogeneity and uniformity of physical properties (in crystal and also in mass), possesses a low wearability factor.

Heat Conduction in Metals. W. Hollies. (Engineering and Boiler House Review, 1943, vol. 57, Sept., pp. 249-252). The author reviews published information on heat conduction in metals. The carbon content of steel has a considerable effect on the variation of the thermal conductivity with the temperature. R. W. Powell has shown that, whereas at 0° C. the thermal conductivity of iron and steel varies from about 0.19 to 0.026 g.cal. per sec. per cm. per °C., the conductivity values merge together at higher temperatures, so that the conductivities of the various steels range only from 0.08 to 0.05 at 700° C. The phenomenon of thermal conduction through a metal under the influence of a higher temperature difference is explained by the fact that the increase in electron speed at the heated surface is transferred by a kind of chain action to progressively distant electrons. The pressure of foreign atoms will cause a distortion of the original lattice possessed by the pure metal and will destroy its periodicity. For this reason, the thermal conductivity of an alloy will always be smaller than that of the pure metal.

The Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steel at 400 to 600°. Marion H. Armbruster. (Journal of the American Chemical Society, 1943, vol. 65, June, pp. 1043-1054). The author describes an investigation of the solubility of hydrogen in substantially pure iron and nickel and in a number of steels at hydrogen pressures ranging from 0.001 mm. to 1.5 mm., at temperatures of 400°, 500° and 600° C.; in the case of iron at 600° C. the pressure range was extended to 350 mm. At each temperature, the measured solubility s is accurately represented, within the experimental error, by the linear equation $s/p^{\frac{1}{2}} = \text{a constant}$ and p is the

pressure of hydrogen; the measurements on iron and nickel at all three temperatures are accurately reproduced by the equations:

$$\begin{aligned}\log (s/p^{\frac{1}{2}}) &= -1454/T + 1.946 \\ \log (s/p^{\frac{1}{2}}) &= -645/T + 1.732\end{aligned}$$

respectively, in which T is the absolute temperature. The results show that, at the pressures and temperatures investigated, the solubility of hydrogen in a ferritic steel does not differ greatly from that in pure iron, whereas in an austenitic steel the solubility is four or five times as great, and is about the same as in pure nickel. Comparison by extrapolation of the new results with data in the literature shows a general accord, particularly at temperatures of 600° C. and higher.

Boron plus Titanium in Heat-Treated Steels. G. F. Comstock. (Metals and Alloys, 1943, vol. 17, May, pp. 978-983). The author studies the properties of steels treated with the ferrous alloys Bortam and Carbortam, both of which contain boron and titanium. The hardenability, or depth of hardening, of these steels is raised by an amount equivalent to that obtained by an increase of 0.7% in the manganese, or 1.6% in the silicon, or 0.20-0.25% of molybdenum. When the tensile and impact properties are compared after quenching and tempering at temperatures not over 600° F., the boron-treated steels are practically as strong as similar untreated steels with about 0.25% of molybdenum, and are tougher and at least as ductile; but when compared, after quenching and tempering at 900° F., with the molybdenum steels, the latter are appreciably stronger though less ductile and tough. The use of titanium rather than zirconium with boron is found to be advantageous.

User Report No. 14 on Experience with NE (National Emergency) Alloy Steels. F. Horak and E. Champlin. (Steel, 1943, vol. 112, June 7, pp. 106-108; June 14, pp. 99, 126; June 21, pp. 92-94). The authors report the results of tests on and their experience with several of the 8000 series of National Emergency steels.

Intensifying of NE 9440 Steel. (Iron Age, 1943, vol. 152, July 1, pp. 56-57). Data are presented on the improvements in hardenability, tensile properties and impact strength obtained in NE 9440 steel (a low-alloy chromium-nickel-molybdenum steel) by treating the ingots with 4 lb. of Grainal per ton of steel. The composition of Grainal is not given.

Carbon and Alloy Steels for War Purposes. (Metallurgia, 1943, vol. 28, July, pp. 123-126). A considerable degree of rationalisation of carbon and alloy steels has taken place to meet war-time conditions. In this paper a number of British and American specifications and schedules of steels are reviewed.

Guide for the Selection of Tool Steel. W. E. Bruse. (Iron Age, 1943, vol. 151, June 24, pp. 63-68). The author discusses the characteristics and specifications of the tungsten, molybdenum and cobalt types of high-speed steel, of air-hardening and oil-hardening steels and of cemented carbides.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 172 A-176 A)

Testing with X-Ray Counting Tubes. (TZ für praktische Metallbearbeitung: Iron Age, 1943, vol. 151, June 10, pp. 70-71, 120). A brief description is given of German developments in making quantitative intensity measurements of X-rays by means of Geiger-Müller counting tubes. The counting tube gives a measured value in terms of the mean radiation intensity across the whole field, the size of which is governed by the counting-tube diaphragm opening. Generally speaking, the field should not be smaller than 1 sq. cm. to make the investigation of large areas of metal economically possible. Steel up to about 2 in. thick can be measured with an accuracy of 0.5% using a measuring area of 2 sq. cm. and a measuring time of 0.1 sec. The technique is suitable for testing lined chemical equipment, such as retorts, for the progress of corrosion can be determined without removing the lining.

Austenite Determination in Heat Treated Steels. F. S. Gardner, M. Cohen and D. P. Antia. (American Institute of Mining and Metallurgical Engineers: Heat Treating and Forging, 1943, vol. 29, Mar., pp. 143-146; May, pp. 245-246). The authors describe an X-ray diffraction method of determining the amount of retained austenite in steel. In order to cancel out the effect of uncontrollable variations in the X-ray exposure and film-development conditions, a standard reference line is superimposed on each film by maintaining a piece of aluminium foil in the path of the incident X-ray beam during the entire exposure. With different samples of steel and the same field, the ratio of the density of any one austenite line to the density of the reference line is a function of the retained austenite content.

Determination of Austenitic Grain Size. C. Petteford. (Iron and Steel, 1943, vol. 16, Aug., pp. 496-499). After discussing factors which affect the size of austenite grains in heated steel the author describes microscopical and fracture methods of determining their size. The McQuaid-Ehn and the oxidation methods, in which the composition of the steel at the surface is changed, have both been standardised by the American Steel Standardisation Group. Methods which do not involve changes in composition consist of outlining the former austenite grains with decomposition products by using suitable cooling speeds, or of developing "footprints" of the austenite grain size in martensite with special etching reagents.

Effect of Inhomogeneity of Austenite on the Rate of the Austenite-Pearlite Reaction in Plain Carbon Steels. G. A. Roberts and R. F. Mehl. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1568: Metals Technology, 1943, vol. 10, June). The authors attempt to evaluate quantitatively the effect of

heterogeneity upon the rate of the austenite-pearlite reaction in plain carbon steels and propose a method for determining the austenitising heat-treatment cycle necessary to obtain "practical homogenisation." By the measurement of but two quantities, the fracture grain size and the time for half of the austenite to be transformed at a sub-critical temperature near the A_{e1} point, fracture-grain-size/half-reaction-time curves are prepared. A calculation is first made of the theoretical change in the austenite grain size when the austenite is homogeneous; this change is represented by a straight line when plotted as a fracture-grain-size/half-reaction-time curve. Curves are also constructed from experimental data for specimens having different degrees of heterogeneity as a result of holding at the austenitising temperature for different periods of time. For any steel, the point at which the slope of this curve becomes the same as that of the straight line (the calculated curve for a fully homogeneous specimen) indicates the minimum austenitising time necessary to produce complete homogeneity. A means is thus provided for preparing homogenisation schedules for equivalent homogeneity in steels with different homogenising characteristics. If steels are austenitised for lengths of time dictated by the above procedure, no effect of minor heterogeneity should be found in the reactions at temperatures near the A_{e1} point, in the reactions at temperatures near the knee of the S-curve, or in the hardenability.

The Metallurgy of Modern Alloys. R. H. Harrington. (Heat Treating and Forging, 1943, vol. 29, June, pp. 282-284, 302; July, pp. 336-338, 350). Continuing Part II. of this series of articles (see p. 133 A), the author in this section explains and gives examples of equilibrium diagrams of the principal types of solid phase reactions which are fundamental to the heat treatment of metals.

The Thermal Diagram of the System Iron-Tin. W. F. Ehret and D. H. Gurinsky. (Journal of the American Chemical Society, 1943, vol. 65, June, pp. 1226-1230). The authors investigated the Fe-Sn system at temperatures above 500°C . and in the range of 10% to 100% of tin. A new phase diagram was set up from the results obtained; this confirms the earlier diagram of Ehret and Westgren and gives definite temperature intervals of stability for the several intermetallic phases. Lattice constants are given for the five intermediate phases, namely, Fe_2Sn , Fe_3Sn_2 , γ -phase (with a NiAs structure), FeSn and FeSn_2 .

CORROSION OF IRON AND STEEL

(Continued from pp. 176 A-177 A)

The Corrosion of Metals in Air. W. H. J. Vernon. (Chemistry and Industry, 1943, vol. 62, Aug. 21, pp. 314-318). The author reviews some of the results of corrosion investigations at the Chemical

Research Laboratory, Teddington, during the last two decades. Contrary to the popular belief, a clean iron surface will rust freely in an ordinary room atmosphere of low relative humidity. Rusting proceeds from sporadically distributed centres having no relation to any factor connected with the metal itself. The number of centres increases with time. Specimens exposed in a muslin cage remained entirely free from rust whilst control specimens exposed immediately outside rusted freely. Nuclei for the rust centres were therefore provided by disperse solid particles in the atmosphere. The rate of attack due to disperse particles at low relative humidities falls off as the available unattacked areas become reduced. At increased humidities a point is reached at a relative humidity of about 70% when an enormous increase in the rate of rusting occurs. This phenomenon is an indirect effect due to a property of the previously formed crust. Specimens were inoculated with particles of ammonium sulphate, others with silica, and others with charcoal, and exposed either to purified air, or to air containing a little sulphur dioxide; the relative humidity was gradually increased to 99% in 32 days, at which it was kept for a further 68 days; the weight increments due to rusting were measured. Although the system was below saturation for the whole period, the first critical humidity occurred in about 20 days, at a relative humidity of 50-65%; this indicated the beginning of the attack on the metal with the breakdown of the air-formed film. No serious corrosion occurred even with prolonged exposure at this humidity. At the secondary critical humidity, approximately 80%, a relatively enormous increase in corrosion occurred with the production of ordinary red rust. Particles of ammonium sulphate are intrinsically effective in promoting attack with no sulphur dioxide in the atmosphere, whilst charcoal has no intrinsic effect, but becomes enormously active in the presence of traces of sulphur dioxide. No evidence has been found to support the belief that carbon dioxide permits corrosion to go on indefinitely; on the contrary, atmospheric carbon dioxide has a marked repressive effect.

Furnace Tube Corrosion. (Journal of the Institute of Fuel, 1943, vol. 16, Aug., pp. 177-181). This is the Final Report of the Special Committee acting under instructions of the Boilers and Combustion Sub-Committee of the Prime Movers' Committee appointed by the Edison Electric Institute. The Report covers the investigation of the cause and remedy for the wastage of the outer surface of tubes occurring in many power-station wet-bottom boiler furnaces. In the presence of a reducing atmosphere, wastage of metal from tubes may take place by the formation of compounds of relatively low melting points, such as iron-sulphide/iron-oxide or other complex eutectics between the metal and the outside layer, which ultimately results in intercrystalline penetration into the tube surface. The ultimate solution to the problem is to design the burner so as to ensure maintenance of fuel ignition close to the

burner and at the same time to see that there is sufficient oxygen in the furnace atmosphere for it to be adjacent at all times to the walls where the flame is propagated.

ANALYSIS

(Continued from pp. 96 A-99 A)

Standard Sampling Methods. (Steel, 1943, vol. 112, May 17, pp. 128, 148). Particulars are given of the methods recommended by the American Iron and Steel Institute for taking samples of drillings or chips from steel of different shapes and sizes.

The Spectrographic Analysis of Cast Iron. F. B. Ling, J. McPheat and J. Arnott. (Institute of British Foundrymen, 40th Annual Conference, June, 1943, Paper No. 771; Foundry Trade Journal, 1943, vol. 70, July 22, pp. 233-238, 240). The authors describe a large-size Hilger quartz spectrograph at the foundry of G. and J. Weir Ltd., and the technique employed for making determinations of the elements in cast iron. The advantages of this method are the speed with which the results are obtained, that the samples are easily prepared and that a permanent record is made. The disadvantages are that it can be applied only to the estimation of elements the log-ratio curves of which are known, that there is a definite upper limit to the amount of an element which can be determined, that unsatisfactory results are obtained from heterogeneous samples owing to the minute size of the areas sparked, and that it is not applicable to drillings.

Determination of Iron in the Presence of Chromium and Titanium with the Jones Reductor. F. S. Grimaldi, R. E. Stevens and M. K. Carron. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, June, pp. 387-388). The authors describe a method of determining the amount of iron in a sulphuric acid solution when chromium and titanium are also present. Sulphuric acid solutions of titanous and chromous sulphates, obtained by passing the solution to be tested through a Jones reductor, are oxidised by aeration for from 5 to 10 min. in the presence of a trace of copper sulphate as a catalyst. Ferrous sulphate is essentially unoxidised and is titrated with permanganate after aeration.

Determination of Small Amounts of Molybdenum in Tungsten and Molybdenum Ores. F. S. Grimaldi and R. C. Wells. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, May, pp. 315-316). A rapid method has been developed for the determination of small amounts of molybdenum in tungsten and molybdenum ores. After removing iron and other major constituents the molybdenum thiocyanate colour is developed in water-acetone solutions, using ammonium citrate to eliminate the interference of tungsten.

The Rapid Photometric Determination of Copper in Ferrous Materials. F. W. Haywood and A. A. R. Wood. (*Analyst*, 1943, vol. 68, July, pp. 206-208). The authors describe a rapid and accurate method for the determination of copper in ferrous alloys by measurement of the absorption of the golden colour produced in the interaction of copper salts and diethyldithiocarbamate. The interference of nickel is overcome by the rapid removal of nickel salts with dimethylglyoxime. The determination in a steel or cast iron containing nickel can be effected in 15-20 min. after initial solution.

The Training of Female Assistants for Steelworks Laboratories. M. B. Thompson and R. Belcher. (*Metallurgia*, 1943, vol. 28, July, pp. 101-104). At the request of the Ministry of Labour and the Board of Education, courses for the training of female assistants for steelworks laboratories are being held in the Metallurgical Department of the Rotherham College of Technology and Art. Details of the method of training are given together with a general discussion of the results obtainable. As to the probable suitability of a girl for this class of work, the experience gained showed that: (1) Previous experience is not important; (2) age, and time since leaving school are unimportant, at least up to 26; (3) secondary education is desirable; (4) previous knowledge of chemistry is immaterial; (5) the most important factors seem to be general intelligence and quick-wittedness, allied to reasonable manual dexterity.

Recent Developments in Laboratory Apparatus. R. H. Powell. (*Iron and Steel*, 1943, vol. 16, June, pp. 428-431; July, pp. 468-470, 477). The author describes modern laboratory apparatus for the sampling and analysing of solid fuel and coke-oven gas, a portable CO₂ meter, a microid balance desiccator, a modified Ströhlein apparatus for carbon estimations and some forms of electro-chemical analysis apparatus.

Statistical Study of the Precision of Methods for Analysis of Coal and Coke. H. H. Lowry and C. O. Junge, jun. (*Proceedings of the American Society for Testing Materials*, 1942, vol. 42, pp. 870-885). The authors report on a statistical analysis of the results obtained by 19 organisations making 176 sets of determinations, including over 32,000 analyses of coal and coke by the standard A.S.T.M. procedures. The precision of the determinations varied by fairly large factors for the different laboratories. On the assumption that the permissible difference between duplicates should have a value such that a third determination would not have to be made more than 50 times per 1000 samples, the permissible "most precise laboratory" and "reasonable" differences were calculated.

Microdetermination of Volatile Matter in Coal and Coal Products. M. Neuworth and W. R. Kirner. (*Industrial and Engineering Chemistry, Analytical Edition*, 1943, vol. 15, May, pp. 359-360). To study the combustion of pulverised coal it was necessary to determine the volatile matter in very small samples. The authors

describe a method which consists of carbonising a 3-mg. sample in a platinum boat in a quartz combustion tube under nitrogen. The sample is introduced into a cold part of the tube; the heating rate is high, and cooling takes place in an oxygen-free atmosphere. Statistical analysis of the results obtained on 43 samples proved that they were as reproducible as those obtained by the A.S.T.M. method.

The Proximate Analysis of Coal. J. Brown and A. S. Bean. (Journal of the Institute of Fuel, 1943, vol. 16, Apr., pp. 103-114). The authors review and discuss methods of making proximate analyses of coal. It is regretted that in the British Standard method of determining the volatile matter (B.S. 1016) the temperature has been reduced from $965^{\circ}\text{C.} \pm 15^{\circ}\text{C.}$ to 925°C. with no tolerance, for now gas coals lying at the lower end of the 32% class, for example, will fall into the 31% class. The arrangement of apparatus, procedure and method of reporting proximate analyses at the laboratory with which the authors are connected are described. Information of the greatest value can be obtained only by consideration of a *series* of analyses of any given coal. The proximate analysis can be used to select a number of likely coals; then all possible additional tests should be used to settle the various characteristics—one at a time.

Coal Analyses and Their Relation to Combustion Characteristics. J. L. G. Weysser. (Illinois University, Engineering Experiment Station, 1942, Circular Series No. 43, pp. 72-82). The author defines the terms vitrain, clarain, durain and fusain and reviews methods of making ultimate and proximate analyses of coal.

SUBJECT INDEX.

[References to the papers read before the Institute are indicated by the word *Paper* following the page number. The letter *P.* denotes a reference in Section I. of the Journal which contains the reports of the proceedings of meetings, the papers read, and the discussions thereon. The letter *A.* denotes a reference to the section dealing with abstracts.

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